

THE ANALYTICAL CHEMISTRY OF
TANTALUM AND NIOBIUM

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THE ANALYSIS OF
THEIR MINERALS AND THE APPLICATION
OF TANNIN IN GRAVIMETRIC ANALYSIS

Based upon Original Researches

BY
W. R. SCHOELLER

PH.D. (GREIFSWALD), FELLOW OF THE INSTITUTE OF CHEMISTRY.
MEMBER OF THE SOCIETY OF PUBLIC ANALYSTS AND OF THE
MINERALOGICAL SOCIETY. LATE LECTURER IN MINERALOGY AT
THE SIR JOHN CASS TECHNICAL INSTITUTE. RECIPIENT OF THE
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With a Foreword by G. ROCHE LYNCH, O.B.E.,
M.B., B.S.(Lond.), D.P.H.(Eng.), F.I.C., Senior
Official Analyst to the Home Office

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FOREWORD

I AM greatly honoured by the request of Dr. Schoeller to write, as President of the Society of Public Analysts and other Analytical Chemists, a foreword to his monograph on the Analytical Chemistry of Tantalum and Niobium. The Society is proud to publish this monograph under its auspices, for in addition to being a critical essay on earth-acid analysis, it elaborates the results of Dr. Schoeller's work, some 33 original papers, all of which with one exception appeared in the Journal of the Society, *The Analyst*; the work has for twelve years been carried out under the Analytical Investigation Scheme of the Society. Dr. Schoeller's investigations, ably assisted by many collaborators, have taken some seventeen years. Great difficulties have been encountered, difficulties that might have disheartened many of us, but the perseverance of this team, so ably presided over by Dr. Schoeller, has brought to fruition a fine piece of work that, apart from its analytical importance, might well serve as an example of patience and industry to all. The bulk of the work was done at the Sir John Cass Institute, where Dr. Schoeller was fortunate enough to obtain laboratory space, and where it was his custom to repair in the evenings and work for some four hours after the day's routine work had been done.

At the outset they were faced with many obstacles. The recognised methods, copied from book to book, were tested and found wanting. Entirely new methods, therefore, had to be devised. In the course of the work their introduction of tannin for the separation of the earths proved to be a vital factor in the solution of the problem, and it seems probable that this substance will have other applications in inorganic analysis. The work of Dr. Schoeller and his collaborators is now recognised abroad and references to his work are to be found both in English and foreign publications. Though "finis" can never be put to any analytical process, it is true to assert that reliable methods are now available in this particular branch of inorganic analysis.

FOREWORD

It is, in conclusion, a pleasure to state that this work has already received signal recognition, for in 1932 Dr. Schoeller was one of the recipients of the Sir George Beilby Award, which is given each year for the most outstanding research in metallurgical chemistry.

G. ROCHE LYNCH.

DEPARTMENT OF CHEMICAL PATHOLOGY,
ST. MARY'S HOSPITAL, W.2.
31st May, 1937.

AUTHOR'S PREFACE

THE text of this compact little volume is based upon the researches of a team of workers which it was my privilege to captain. The results of our work—most of which was carried out in the Sir John Cass Technical Institute—are recorded in a series of papers published in *The Analyst* under the general title, "Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates."

Long before we had fully mapped out the virgin ground discovered at the price of several years' arduous exploration, I realised that our original papers would not prove a suitable guide to the practice of earth-acid analysis. The systematic treatment of the subject would require an entire re-arrangement of the published data as well as excision of some of our earlier procedures since greatly improved by progressive refinement in our methods.

In writing this monograph I have carefully sifted the text of the *Investigations*; it should be emphasised, however, that—with the exception of Chapter IV on Analytical Technique (substantially a reprint of Sections VI and XIX)—the present work is practically a new production. It describes all the analytical methods given in our papers, but welded into a comprehensive analytical scheme now published for the first time, after additional experimental work not recorded in the *Investigations* (Chapters V to XII). This part of the work treats of fundamental propositions of analytical chemistry, viz., the quantitative separation and determination of a large number of rarer and other elements, hence its scope is by no means confined to earth-acid analysis. I am well aware that the last word on this scheme has not been spoken, therefore I shall be grateful for any criticisms and suggestions aiming at its improvement. The new structure, laboriously erected by willing hands, may disclose a few minor flaws requiring further attention; but I have faith in its foundations, which will prove to have been well and truly laid.

AUTHOR'S PREFACE

Part III is, in the main, a small separate monograph on the recent analytical applications of tannin, in which our own and other workers' methods are compiled, and theoretical considerations on the action of the reagent submitted.

I have much pleasure in acknowledging the valuable help of Dr. Roger C. Wells, Chief Chemist of the U.S. Geological Survey, Washington, who courteously revised the text of the hydrofluoric-acid method (§§ 30 to 32) and contributed data on the ammonia precipitation of the rare earths (§ 87); and of my collaborator, Mr. A. R. Powell, in supplying details of his procedures for the cupferron method (§ 65) and the precipitation of the rare earths by ammonia and tannin (§ 87). I am greatly indebted to Dr. G. Roche Lynch, O.B.E., M.B., F.I.C., President of the Society of Public Analysts, and the members of his Council, for according me their support towards the publication of this work under the Society's auspices.

W. R. S.

LONDON,
May, 1937.

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DEFINITIONS

Earth Acids. This time-honoured expression is used in the singular or plural as a convenient generic term, to denote the pentoxides of tantalum and niobium, either anhydrous or hydrated. It does not include tungstic or titanic acid.

Metallic Acids. Collective term embracing tantalic, niobic, tungstic and titanic acids or oxides.

Pentoxides. When used without qualification, this term stands for the oxides Ta_2O_5 and Nb_2O_5 .

Dioxide Earths. Titania, zirconia, hafnia, thoria.

Rare Earths. Oxides of the cerium, terbium and yttrium groups (excluding scandia and thoria).

Earths. Comprises pentoxide, dioxide and rare earths, as well as alumina and beryllia ; excludes alkaline earths.

NOTE ON REFERENCES

The reference numbers in Roman numerals (I.-XXXIII.) found in the text without corresponding footnotes, are the sectional numbers of our thirty-three papers on tantalum, niobium, etc., summarised in Chapter XVI.

The work of W. F. Hillebrand and G. E. F. Lundell, repeatedly cited in the text, is entitled *Applied Inorganic Analysis* (New York : John Wiley & Sons Inc. ; London : Chapman & Hall Ltd., 1929).

References to other authors' works and memoirs are given in footnotes in the customary manner.

THE ANALYTICAL CHEMISTRY OF TANTALUM AND NIOBIUM

CHAPTER I

HISTORICAL NOTE

THE principal obstacles which have hindered progress in earth-acid analysis are the weakly defined chemical deportment of tantalum and niobium, their remarkably close resemblance, and the complexity of the greater number of their minerals.

Whilst niobium is slightly more reactive in its compounds than tantalum, the earth acids are more indifferent in chemical reactivity than any of the other earths. No simple stable compounds, such as soluble or insoluble chlorides, nitrates, sulphates, or sulphides, no quantitative stoichiometric reactions producing precipitates of definite composition, are available for analytical work. The fluorides of tantalum and niobium, the tantalates and niobates of potassium and sodium, are analytically useful, but of very limited applicability. All earth-acid compounds show a more or less pronounced tendency to undergo hydrolytic decomposition; such balanced reactions, which do not readily proceed to completion, give rise to colloidal suspensions of the hydrated oxides. Prior to the development of colloid chemistry, these imperfectly flocculated precipitates were the bane of the analyst, whose work they vitiated through incomplete precipitation, contamination by adsorption, slow filtration, and cloudiness of filtrate.

The close similarity in the reactions of tantalum and niobium, which has defeated all attempts at a clean-cut analytical separation, is too well known to require further elaboration; it is the frequent association of a third oxide—titania—with the earth acids that has provided one of the most baffling problems in the whole range of analytical chemistry. Not only is it impossible to separate tantalum from niobium in presence of more than insignificant amounts of titanium, but the quantitative separation of titania from the earth acids is an undertaking which has thwarted the efforts of every investigator during the past century.

DISCOVERY OF THE EARTH ACIDS

These failures are now understood to have been due to the formation of colloidal mixtures resulting in complex precipitates, an effect of association long known as "loss of individuality."¹

On account of the constant association of tantalum and niobium in isomorphous admixture and the regular presence of certain minor associates such as tin, tungsten and titanium, the resolution even of the simpler earth-acid minerals into their constituents is a difficult proposition of qualitative analysis; but when it comes to the group of the native titanoniobates, the mineralogist is actually confronted with some of the most complex products of inorganic Nature. In addition to every known earth, a number of rare elements, heavy metals and common bases have been identified in the various members of this class of bodies.

The correct interpretation of all the facts bearing on the analytical chemistry of the earth acids and certain associated metals has necessitated the labours of several generations of chemists. Hence it is not surprising that a long period of uncertainty and confusion followed the discovery of "Columbium" by Hatchett² (1801) and of "Tantalum" by Ekeberg³ (1802). As neither investigator was aware of the exact nature of the mixed earth acids isolated by him, it is not historically correct to represent the former as the discoverer of columbium (or niobium), or the latter as the discoverer of tantalum. The history of the discovery of tantalum and niobium began with Hatchett's analysis of columbite and ended with Marignac's epoch-making researches (1866). In the meantime some of the most famous scientists of the period strove to solve the problem of the composition of earth-acid minerals. Wollaston,⁴ in 1809, believed he had established the identity of Hatchett's columbic with Ekeberg's tantalic acid. Berzelius⁵ (1820) studied the properties of the acid extracted from tantalite and prepared tantalum in an impure state; his illustrious friend Wöhler⁶ (1839) investigated columbite and pyrochlore without reaching any definite conclusions as to the identity of the metallic acids contained in these minerals.

In the course of his extensive researches (1844-1853), H. Rose⁷ endeavoured to differentiate three kinds of earth acid, namely, Berzelius's "tantalic" acid and the acids of two new elements,

¹ Crookes, *Select Methods in Chemical Analysis*, London, 1905, p. 139.

² *Phil. Trans.*, 1802, 92, 49.

³ *Ann. Chim.*, 1802, 43, 276.

⁴ *Phil. Trans.*, 1809, 99, 246.

⁵ *Pogg. Ann.*, 1820, 4, 6.

⁶ *Ibid.*, 1839, 48, 91.

⁷ *Ibid.*, 1844, 63, 307, 693; 1846, 69, 118.

MARIGNAC'S INVESTIGATIONS

niobium and pelopium. Later, when his own work had led him to reject the possibility of the existence of pelopium, he still held that niobium was capable of forming two distinct acids, "hypo-niobic" and "niobic." Judging by Rose's statements, his "niobic" acid must have been a mixture of niobic and tantallic acids, his "hyponiobic" a much purer form of niobic acid. On the other hand, he seems to have succeeded in preparing practically pure tantallic acid.

R. Hermann, an indefatigable worker, published numerous papers ¹ on the earth acids and their minerals (1846-72). Although he was able to prove the simultaneous occurrence of tantalum and niobium in a number of minerals, most of his analytical work is only of historic interest. His researches on the metallic acids obtained from certain titanoniobates led him to announce the discovery of two new elements, ilmenium and, later on, neptunium. To the last he defended his views on the individuality of ilmenium against his formidable antagonist Marignac, who pronounced "ilmenic acid" to be a mixture of niobic and titanlic acids.

One other name has to be added to the list of defunct "elements" stated to have been discovered in earth-acid minerals, namely, von Kobell's dianium ² (1860). This appears to have been identical with niobium.

The classic investigations of Marignac mark the beginning of a new phase in the chemistry of the earth acids. In his two memoirs, *Recherches sur les Combinaisons du Niobium* ³ and *Recherches sur les Combinaisons du Tantale*, ⁴ he definitely characterised the two metals as closely related, distinct elements, and determined the composition of their alkali salts and complex fluorides, expressing it in the now customary formulæ based on the quinquivalency of the two elements. Further, he described the well-known separation method based upon the sparing solubility of potassium fluorotantalate, which he applied to the analysis of a number of minerals. This enabled him to deny the existence of ilmenium and dianium. Marignac's conclusions were confirmed by the work of Blomstrand ⁵ and of Ste. Claire Deville and Troost ⁶ on the composition and vapour density of the chlorides.

In the light of this brief historical survey, it will, I think, be

¹ *J. prakt. Chem.*, 1846, 38, to 1872, 5.

² *J.B.*, 1860, 150; 1861, 210.

³ *Ann. Chim. Phys.*, 1866, 8, 5.

⁴ *Ibid.*, 1866, 9, 249.

⁵ *J. prakt. Chem.*, 1866, 99, 44.

⁶ *Compt. rend.*, 1865, 60, 1221.

UNSOLVED PROBLEMS

conceded that the adoption of the term niobium for columbium is justified. Those investigators to whose experiments and discussions we owe our present knowledge of its elementary character, called it niobium; and whilst Rose, who coined the word, was not altogether correct in his observations, we pay tribute to the genius of Marignac when we use the term which he applied to the element.

The strenuous controversies which resulted in such important additions to our knowledge of the elements were followed by a prolonged period of quiescence, during which no advance in the analytical chemistry of the earth acids was made. The acidic earths contained in the minerals under discussion had been defined qualitatively; the problem of their quantitative determination remained. The separation of titania from the earth acids proved the main obstacle, which even Marignac was unable to overcome. In his memoir, *Essais sur la Séparation de l'Acide Niobique et de l'Acide Titanique*,¹ he concluded that the four methods examined by him were inaccurate.

No further research of analytical importance appears to have been made until the opening years of the present century. From 1904 to 1908, E. F. Smith and his students published a number of papers on the compounds of tantalum and niobium in which some of the established analytical methods were criticised as having proved inaccurate; but they achieved no progress towards greater accuracy. As to the titanium problem, Smith² expressed himself as follows: "how to free the columbium from titanic acid we do not know. We are in precisely the same position as that of Marignac, notwithstanding we have probably made greater efforts than he to remove it from the columbium. Warren³ (1906) was equally pessimistic.

A publication by Weiss and Landecker⁴ (1909) led to several criticisms of the two methods they proposed, (1) for the separation of titania from the earth acids, by fusion of the mixed oxides with sodium carbonate and nitrate, and extraction with hot water; and (2) for the separation of tantalum from niobium by the same fusion process, supplemented by treatment of the aqueous extract with carbon dioxide. The favourable results claimed by Weiss and Landecker could not be reproduced, and for reasons given in Chapter II, I have no doubt that both methods are unsound in principle.

¹ *Arch. Sc. phys. et nat.*, 1867, 29, 265.

² *Proc. Amer. Phil. Soc.*, 1905, 44, 151, 177.

³ *Chem. News*, 1906, 94, 298.

⁴ *Z. anorg. Chem.*, 1909, 64, 65.

RECENT RESEARCHES

The first step towards a solution of the major problem of earth-acid analysis was taken by Dittrich and Freund ¹ (1908) when they applied the ready complex-formation of titanium with salicylic acid to the separation of titania from zirconia and thoria. Hauser and his collaborators ² (1909–1910) endeavoured to extend this reaction to the separation of titania from the earth acids, but must have been unsuccessful; this is an inference drawn from the internal evidence afforded by Meyer and Hauser's monograph, *Die Analyse der seltenen Erden und der Erdsäuren* (Stuttgart, 1912), in which, for no stated reason, the earlier procedure has been omitted and replaced by Muller's salicylic acid method ³ (1911). The latter was definitely superior to any of the earlier methods, but tedious and inaccurate, resulting in a serious loss of earth acid. Hauser's failure is easily understood, as he applied a procedure which I hold to be faulty in principle, namely, selective extraction of the titania from a complex precipitate.⁴

The publication of Meyer and Hauser's monograph may be regarded as the concluding event in the second period of the history of earth-acid analysis. A study of this compilation shows how little had been accomplished in the preceding forty years. Well might the authors say (p. 177): "the chemistry of niobium and tantalum is even yet so undeveloped that the analytical methods for their detection and separation are beset with uncertainties at every turn."

In 1919 Mr. A. R. Powell and I began to investigate the analytical chemistry of tantalum, niobium, and their mineral associates. As the work progressed we enrolled the help of four more collaborators: Messrs. E. F. Waterhouse, E. C. Deering, B.Sc., C. Jahn and H. W. Webb. The plan laid down was to convert the earth acids into soluble organic (*e.g.*, tartaric, oxalic) complexes—a procedure by which they could be obtained in solution along with their mineral associates—and to devise analytical schemes applicable to solutions of this description. The experimental work required for the full elaboration of this plan occupied seventeen years, the results being recorded in thirty-three sections, published in the form of twenty-eight papers.

The analytical application of the organic acid-complexes led to the most important of our discoveries, namely, that tannin is capable of quantitatively precipitating the earth acids, as well

¹ *Ibid.*, 1908, 56, 344.

² Hauser and Herzfeld, *Zentr. Min.*, 1910, 758.

³ *J. Amer. Chem. Soc.*, 1911, 33, 1506.

⁴ See Chapter II, 4 (p. 14).

PLAN OF PRESENT WORK

as all the other earths, from tartrate or oxalate solutions ; further, that some of the hitherto most perplexing separations (including that of tantalum from niobium) are easily performed by the judicious use of the same reagent under standardised conditions, and that the characteristic coloration of some of the tannin precipitates is of great practical usefulness as an indicator for the progress of such separations. I now regard tannin as the most indispensable reagent for the earths in general and the earth acids in particular.

The separation of the earth acids from all their regular mineral associates was investigated ; we worked out processes substantially as accurate as those employed in other branches of mineral analysis. This applies also to the separation of titania from the earth acids, which we achieved by the action of sodium salicylate upon the oxalate solution of the three oxides. The treatment of that solution with calcium chloride precipitates the earth acids, the coloured salicylic titanium complex remaining dissolved.

Two other procedures for the same separation were also published, as well as new, sensitive tests for the joint detection of the earth acids and their separate identification. Tannin was found to be a suitable reagent for micro-work.

In compiling this monograph I have adopted the following plan. The analytically important compounds of tantalum and niobium, and certain theoretical considerations of fundamental importance in earth-acid analysis, are dealt with in Chapter II. The next chapter gives a very brief survey of the minerals containing tantalum and niobium, with representative analyses reproduced from the literature. It is intended chiefly as a guide to the qualitative composition of the minerals, the greater part of the quantitative data requiring verification. Chapter IV contains manipulative details of the technique evolved in the course of our investigations. The methods for the analysis of earth-acid minerals are described in Chapters V and VI ; the former gives a detailed account of the tartaric-acid method evolved as the result of our researches, the latter is chiefly a compilation of published processes, including J. L. Smith's valuable hydrofluoric-acid method.

The processes described in Part II (Chapters VII to XII) form a consecutive series of operations, the object of which is the quantitative separation of all the elements not removed as sulphides in the tartaric-acid method ; they are the earth acids, dioxide earths, sesquioxide earths, beryllia, and tungstic and uranic oxides. The majority of the separation processes are new,

APPLICATION OF TANNIN

having been worked out and tested in the course of our investigations.

Part III consists of two chapters on the application of tannin in gravimetric analysis, one on qualitative analysis, and a final chapter on the literature of earth-acid analysis. The descriptions of the analytical procedures are interspersed with passages in smaller type, giving abstracts of the investigations that led to the adoption of each procedure, together with results of our test analyses.

PART I

TANTALUM AND NIOBIUM COMPOUNDS
AND MINERALS

ANALYSIS OF EARTH-ACID MINERALS

CHAPTER II

TANTALUM AND NIOBIUM COMPOUNDS OF ANALYTICAL IMPORTANCE

THE study of the earth-acid compounds of analytical importance will be simplified if the corresponding tantalum and niobium compounds are considered together. This brings out their close general resemblance and, at the same time, a more or less appreciable differentiation in their properties. The order in which the compounds are described is that in which they may be derived from the pentoxides by a sequence of analytical operations after fusion with either an alkaline or an acid flux :

(A) By fusion with potassium carbonate and solution of the melt in water, the *pentoxides* furnish a solution of the *potassium salts*. This solution, upon saturation with sodium chloride, gives a crystalline precipitate of the *sodium salts*. The alkali salts are decomposed by mineral acids, with precipitation of the *hydrated earth acids*. Hydrofluoric acid converts this precipitate into soluble *fluorides*, which combine with potassium fluoride to form *complex fluorides*.

(B) When the *pentoxides* have been fused with potassium bisulphate, the product may be dissolved in one of three solvents :
 (1) tartaric acid. This forms the soluble *tartaro-acids* ; tannin precipitates from the solution characteristic *tannin complexes*.
 (2) Oxalic acid converts the earths into soluble *oxalo-acids*, which yield tannin precipitates in the same manner as the tartaro-acids. The oxalic solution, when treated with sodium salicylate and calcium chloride, yields a precipitate containing the *salicylic complexes*.
 (3) Acidified hydrogen peroxide dissolves the melt with formation of the *per-acids*.

The following table reproduces the two series of compounds :

1. Pentoxides.	
<i>A : K₂CO₃ fusion.</i>	<i>B : KHSO₄ fusion.</i>
2. Potassium Salts.	7. Tartaro-acids.
3. Sodium Salts.	8. Oxalo-acids.
4. Hydrated Earth Acids.	9. Tannin Complexes.
5. Fluorides.	10. Salicylic Complexes
6. Complex Fluorides.	11. Per-acids.

It may be noted that the compounds of Series *A* are those

OXIDES—ALKALI SALTS

which were known to the investigators of the nineteenth century, whilst Series *B* includes the compounds used in our new methods of earth-acid analysis.

1. The Pentoxides

Ta_2O_5 , sp. gr. 8.710 Nb_2O_5 , sp. gr. 4.552. These are pure white, amorphous, infusible powders. Pure tantalic oxide remains white on ignition; niobic oxide becomes light-yellow when heated, and returns to its original colour on cooling. The oxides dissolve in molten potassium or sodium carbonate or pyrosulphate, as well as in strong hydrofluoric acid, niobic oxide in all cases more readily than tantalic oxide.

2. Potassium Salts

$4\text{K}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$; $4\text{K}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$. Fusion of the pentoxides with potassium carbonate or hydroxide results in a melt containing potassium "hexatantalate" and "hexaniobate," two isomorphous salts crystallising in monoclinic prisms. As the old prefix "hexa" (denoting the number of Ta or Nb atoms in the formula $\text{K}_8\text{M}_6\text{O}_{19}$) is not sufficiently precise, it is preferable to designate the compounds as 4 : 3 salts, so as to give the ratio of base to acid in the above dualistic formulæ.

Both salts are readily soluble in water and in caustic potash solution; the solution of the niobate in water is practically stable, but the aqueous tantalate solution turns cloudy on being boiled, due to the formation of "acid tantalate," or tantalic acid containing adsorbed alkali. The same effect is produced when the solution is left in contact with the air, the carbon dioxide of which decomposes the tantalate. A current of carbon dioxide passed through the solution effects complete decomposition, with precipitation of tantalic acid. In the case of the niobate solution, carbon dioxide produces a precipitate only after prolonged treatment. The solution of potassium tantalate containing potassium hydroxide is much more stable.

3. Sodium Salts

$4\text{Na}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5$; $7\text{Na}_2\text{O} \cdot 6\text{Nb}_2\text{O}_5$ (water content appears to be variable). When a solution of the potassium salts is saturated with a sodium compound (we always use solid sodium chloride) the earth acids are almost quantitatively precipitated as white, microcrystalline sodium salts.¹ The niobate precipitate forms more readily and is more coarsely crystalline than the tantalate.

¹ Antimony, placed between niobium and tantalum in the 5th Group, gives insoluble sodium antimonate under the same conditions.

HYDRATED EARTH ACIDS

The ratio of base to acid observed by us works out at 4 : 3 for the tantalate and 7 : 6 for the niobate ; the 4 : 3 sodium niobate appears to be incapable of existence.¹ The precipitates which we obtain by treatment of the potassium salt solutions with sodium chloride retain a small, variable amount of potash, bearing no simple molecular relation to the pentoxide ; the more complex sodium niobate was found to be richer in potash than the tantalate.²

The sodium salts are also obtained when the pentoxides are fused with sodium carbonate. Lixiviation of the melt furnishes the sodium salts as a pulverulent residue. Sodium tantalate and niobate are practically insoluble in solutions of high sodium ion concentration, and slightly soluble in water ; the aqueous solutions comport themselves like dilute solutions of the potassium salts (*vide supra*) with regard to stability and precipitation by carbon dioxide.

The individuality of a number of alkali tantalates and niobates described by earlier investigators (see Gmelin-Kraut's *Handbuch der Anorganischen Chemie*, Vol. VI., Part I), must be regarded as doubtful.

4. The Hydrated Earth Acids

$Ta_2O_5 \cdot xH_2O$; $Nb_2O_5 \cdot xH_2O$. The hydrated earth acids are obtained as white, amorphous precipitates when alkali tantalates and niobates are treated with acids, or when tantalum and niobium compounds decompose hydrolytically. No definite formula can be assigned to the hydrated acids ; they consist of the pentoxides in combination with a variable amount of water. In this respect they are constituted like many other "hydroxides," more particularly antimonic, stannic, titanic and tungstic acids, as well as precipitated zirconia, thoria, alumina, etc. Such compounds are substantially similar in their mode of formation and structure, being derived from primary hydrated colloidal particles by decrease in the degree of dispersion, with formation of secondary aggregates. Hence they share the physico-chemical properties of colloidal precipitates, such as coagulation by electrolytes, adsorption, peptisation, ageing, and reciprocal flocculation of sols of opposite sign. Now, when a solution containing compounds of several of these elements undergoes hydrolytic decom-

¹ Cf. Bedford, *J. Amer. Chem. Soc.*, 1905, **27**, 1216.

² We have determined a molecular $K_2O : Na_2O$ ratio of 1 : 13.977 in a tantalate and 1 : 9.720 in a niobate precipitate. Similar observations on the retention of sodium (1 to 2 per cent.) by the cobaltinitrites of rubidium and caesium precipitated by sodium cobaltinitrite have been recorded by Moser and Ritschel (*Monats. Chem.*, 1925, **45**, 13).

HYDRATED EARTH ACIDS

position, it must be assumed that the primary sol particles form by cohesion of structurally similar molecules containing different elements ; in other words, that the primary particles are heterogeneous in a chemical sense. Their structure may be compared to that of a mixed crystal.

If this view is correct, it provides a simple explanation for the marked deviation from specific behaviour caused by the association of two or more hydrated oxides in these colloidal mixtures commonly called complex precipitates. Each individual constituent, more particularly a subordinate one, cannot behave quantitatively towards reagents as it would in the pure state because its molecules are too firmly interlocked with those of another constituent of different chemical reactivity. Thus, a mixed earth-acid precipitate containing more tantallic than niobic acid reacts like tantallic acid. If the reverse is the case, the mixture behaves like niobic acid ; with this difference, that a higher proportion of niobic acid is required to mask the presence of tantalum. This applies also to complex precipitates containing tantallic and titanic acids, while niobic and titanic acids in admixture mask each other more completely than do tantallic and titanic acids. The ternary mixture of tantallic, niobic, and titanic acids presents separation problems which, as related in Chapter I, were still unsolved at the beginning of the present century ; yet the precipitates obtained in the analysis of minerals by the usual hydrolysis method are even more intractable, as they contain several minor constituents in addition to the three principal ones mentioned. Thus, stannic and tungstic oxides are generally present, and their extraction from the hydrolysis precipitate by means of ammonia and ammonium sulphide is incomplete. Again, zirconia strongly modifies the normal behaviour of titania (and *vice versa*) in mixtures of the two oxides ; it also affects that of the earth acids, especially if titania is present as well.

The above considerations on complex precipitates are of great importance, as they assign a common cause to most of the difficulties and complications of earth-acid analysis. In the published methods for the analysis of minerals, the operator is faced almost at the start with a complex hydrolysis precipitate which defies all attempts at a quantitative resolution into its constituents. Similarly, in most of the methods (such as those of Weiss and Landecker and of Hauser, discussed in Chapter I) for the separation of the earth acids from individual associated earths, the treatment involves the production or formation of intractable complex precipitates ; and we cannot conceive of

HYDRATED EARTH ACIDS

any modifications of such processes that would lead to reproducible accurate results.

It may be concluded that if we avoid the formation and manipulation of complex precipitates,¹ and adhere to the principle that *all separation methods must proceed from a common solution of the constituents to be separated*, the degree of accuracy thus attained should be substantially the same as that of the standard analytical methods for the commoner elements. This conclusion has been amply verified by the investigations of which this work is the result.

The hydrated earth acids are quantitatively precipitated in a coarsely flocculent, easily filtrable form when a warm solution or suspension of their alkali salts is acidified with nitric, hydrochloric, or acetic acid and then made slightly ammoniacal. A very weak acid, such as carbon dioxide (see above, under *Potassium Salts*) decomposes the tantalate much more readily than the niobate; while in mixed solutions the precipitation of tantalalic acid by carbon dioxide induces precipitation of niobic acid. We have ascertained that partial neutralisation, *i.e.*, to the bicarbonate stage, of solutions containing alkali tantalate, niobate, carbonate, and chloride, has the same effect as saturation with carbon dioxide; the earth acids are precipitated, the alkali chloride facilitating flocculation of small quantities. The reaction is of analytical value, as alkali tungstate is not decomposed under the same conditions.

The hydrated earth acids are also precipitated, but not quantitatively, when a pyrosulphate melt containing tantalum and niobium is disintegrated by extraction with water; they remain as an insoluble, pulverulent or lumpy residue. Quantitative precipitation may be achieved by prolonged boiling of the solution of the melt, but the completeness of the precipitation is uncertain, and not easily determined. The earth-acid residue retains a variable amount of adsorbed sulphur trioxide, from which it can be freed by repeated ignition with ammonium carbonate or, in the moist state, by digestion with ammonia. In the latter case, however, a certain amount of earth acid (niobic acid to a greater extent) is peptised.

The precipitation of the earth acids from their soluble tartaric

¹ In Section XV (*Analyst*, 1929, 54, 660) I expressed the view that "a molecularly admixed constituent of a complex precipitate cannot be extracted quantitatively by a process of selective solution." In the light of the above discussion, processes based on selective solution must be defective for two reasons: (1) the soluble constituent is imperfectly extracted, and (2) the residual insoluble constituent is more or less peptised as the result of partial solution of the precipitate.

FLUORIDES

and oxalic complexes is discussed below, under 7 and 8 respectively.

5. The Pentafluorides

TaF_5 ; NbF_5 . In the pure state, the pentafluorides form hygroscopic crystals soluble in water. They are fusible and volatile :

TaF_5 : M.P. 96.8° ; B.P. 229.5° C.

NbF_5 : „ $72-73^\circ$; „ $217-220^\circ$ C.

An aqueous solution of the fluorides is readily obtained by treatment of the hydrated earth acids with hydrofluoric acid. The behaviour of such solutions on evaporation, and the volatilisation of tantalum and niobium as fluorides under certain conditions, have long been the subject of conflicting statements in the literature (X.). According to some observers, appreciable amounts of tantalum and niobium (especially the former) volatilise when the fluoride solution is evaporated ; other workers have denied the possibility of volatilisation under such conditions. Hahn and Pütter ¹ have explained these apparent contradictions by showing that volatilisation losses occur only with earth-acid solutions containing alkali fluoride. When solutions of pure tantalum fluoride are evaporated to dryness, the salt is decomposed hydrolytically, and hence the residue is not volatile when ignited. If on the other hand the fluoride solution contains also alkali fluoride, a more stable fluorotantalate is formed which dissociates when ignited, a certain amount of tantalum fluoride volatilising. If the fluoride solution is evaporated with excess of sulphuric acid, no tantalum is volatilised, whether alkali fluoride is present or not. This conclusion is of practical importance, as it justifies the application of the usual evaporation procedure with hydrofluoric and sulphuric acids as a final step in the separation of silica from the earth acids.

6. Complex Fluorides

The only compounds of this class of analytical interest are the following potassium salts : the fluorotantalate, K_2TaF_7 , the fluoroniobate, K_2NbF_7 , and the oxyfluoride $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$.

The fluorotantalate and the fluoroniobate are isomorphous ; they crystallise in orthorhombic needles. The tantalum salt is sparingly soluble in water, which produces a cloudy solution due to partial hydrolysis ; it is stable in very dilute hydrofluoric acid, 200 parts of which dissolve one part of the salt at 15° C.,

¹ *Z. anorg. Chem.*, 1923, 127, 153.

TARTARO-ACIDS

and four parts at 85°. The aqueous solution, when boiled, deposits a precipitate of basic salt.

The fluoroniobate, which is much more soluble than the preceding, is stable only in hydrofluoric acid solution, being decomposed by water with formation of the oxyfluoride: $K_2NbF_7 + H_2O \rightleftharpoons K_2NbOF_5 + 2HF$.

The oxyfluoride crystallises in thin, monoclinic plates, which are soluble in 12 to 13 parts of cold water, much more abundantly in hot water. The dilute aqueous solution deposits a more basic salt only after several hours' boiling.

The complex fluorides are applied in the metallurgy of tantalum, the precipitation of the sparingly soluble fluorotantalate being the only practical means for separating tantalum from niobium on a large scale. Prior to our discovery of the tannin method, it was also the only—though far from perfect—procedure for the analytical separation of the two elements. Its originator, Marignac, succeeded in solving the problem of the identity and separation of the earth acids because he investigated the crystallisable fluorosalts, while most of his contemporaries were attempting the resolution of colloidal, complex precipitates.

7. The Tartaro-Acids

The formation of soluble complexes with the metallic elements is a familiar property of organic hydroxy-acids. The organic complexes of the earth acids, which are of a low degree of complexity, have not been isolated and, with the exception of oxaloniobic acid, their composition is not accurately known.

The tartaro-earth acids are obtained in solution when the bisulphate melt of the pentoxides is dissolved in a hot solution of tartaric acid or ammonium tartrate. The acid solution obtained by leaching with tartaric acid is unstable, the proportion of earth-acid in true molecular solution decreasing with increasing age or dilution. Owing to this slow dissociation the solution, which is quite clear when freshly prepared, will gradually show the Tyndall effect and eventually deposit a colloidal precipitate. The length of time during which the solution remains clear depends upon its history¹ and composition. Thus, tartarotantallic acid is much less stable than the niobium compound. The stability of a mixed earth-acid solution increases with the Nb : Ta ratio ; again, the presence of the tartaric complexes of other elements tends on the whole to have a stabilising effect.

¹ Meticulous care is necessary in its preparation (see Chapter IV, p. 38). I have kept a solution, made from 0.3 g. Ta_2O_5 , 4 g. $KHSO_4$, 4 g. $C_4H_6O_6$, and 100 ml. of water, for as long as four weeks before cloudiness set in.

OXALO-ACIDS

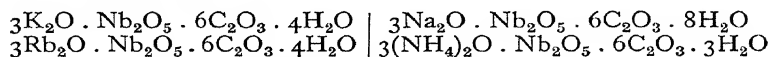
As tartar-emetic solution is precipitated by mineral acids, so the tartaro-earth acids are decomposed when solutions containing them are boiled with strong hydrochloric or nitric acid, the earth acids being almost completely precipitated in a flocculent condition; large amounts of tartaric or sulphuric acid induce less complete precipitation. We use the term "tartaric hydrolysis" for this important and specific reaction.¹ The addition of large quantities of ammonium chloride causes dissociation of the tantalum complex, with formation of a bulky gelatinous precipitate. Caustic alkali at high concentration forms salts of the constituent simple acids, sodium hydroxide causing partial precipitation of the earth acids as sodium salts. The earth acids are quantitatively precipitated by tannin from the neutralised solution of the tartaro-complexes in the form of characteristic, coloured tannin adsorption complexes. Ammonia does not precipitate the solution; in fact, an ammoniacal tartrate solution of the earth acids is more stable than the acid solution.

The *citro-earth acids* are similar in properties to the tartaro-complexes. They are obtained by lixiviation of the bisulphate melt of the pentoxides with citric acid or ammonium citrate; the solution undergoes hydrolysis when boiled with strong hydrochloric acid.

8. The Oxalo-Acids

We obtain a solution of the oxalo-acids by leaching a bisulphate melt of the pentoxides with ammonium oxalate solution; oxalic acid may also be used.

Oxaloniobic acid is the stablest of the earth-acid complexes. It has been investigated by Russ,² who prepared and analysed the following alkali salts:



Its constitution, derived from the above formulæ, is $\text{NbO}(\text{C}_2\text{O}_4\text{H})_3$, which is analogous in type to the stable oxyfluoride NbOF_3 . Tantalum is apparently unable to form a corresponding compound: Russ claims on one occasion to have obtained the potassium salt of the penta-acid $\text{Ta}(\text{C}_2\text{O}_4\text{H})_5$ —analogous to TaF_5 . At any rate, oxalotantallic acid is stable only in presence of free

¹ The dissociation of the soluble tartaric complex of titania by strong mineral acids does not produce a precipitate, soluble titanic chloride or nitrate being formed. The earliest of our methods for the separation of titania from the earth acids is based on this principle (§ 53).

² *Z. anorg. Chem.*, 1902, **31**, 42.

TANNIN COMPLEXES

oxalic acid ; its solution is precipitated by ammonia, whilst oxaloniobic acid solutions are not thus precipitated if sufficiently dilute. In presence of tantalum, however, niobium is quantitatively precipitated (Russ). It is the differential stability of the two compounds in slightly *acid* solution which has enabled us to work out our new tannin method for the separation of tantalum from niobium. Both elements are quantitatively precipitated by tannin from the *neutralised* oxalate solution.

The oxalo-acids are decomposed by boiling with strong hydrochloric or nitric acid, but the precipitation of the earth acids is very incomplete ; the same remark applies to tartaric hydrolysis (*q.v.*, under (7) above) if any oxalic acid is present in the tartrate solution.

9. The Tannin Complexes

These compounds were known to Rose and his contemporaries, who endeavoured to apply the tannin reaction to the characterisation of the constituent earths of earth-acid minerals. Since, however, the test as carried out by them fails when applied to mixed earths, the analytical application of tannin (which had never been thoroughly investigated) fell into disuse after Mari-gnac's successful solution of the identification problem.

As mentioned in Chapter I, we have found in the course of our researches that the tannin complexes can be applied, not only to the identification and determination of tantalum and niobium, but to their quantitative separation from each other and from a number of other earths.

The tannin compounds of tantalum and niobium are adsorption complexes produced by reciprocal flocculation of two colloids of opposite sign, namely, the negative tannin, and the positive earth-acid, sols. The resultant precipitates, though bulky, are very tractable, and the precipitation is quantitative. The pure tantalum complex is of a fine lemon-yellow colour, whilst the niobium complex is bright vermilion ; hence the two precipitates may be compared in appearance to arsenic and antimony sulphide, respectively. The delicate colour of the tantalum precipitate renders it liable to discoloration by co-precipitation of small amounts of other elements ; titanium or tungsten produce a buff colour, iron grey to mauve, niobium a pale orange. This explains why some authors have attributed a light-brown colour to the tantalum precipitate. The colour of the niobium compound is too intense to be affected by subordinate amounts of other elements, with the exception of iron and vanadium.

Rose obtained the tannin complexes by treating alkali tantalate

TANNIN COMPLEXES

or niobate solutions with tannin and acidifying with a mineral acid, the earth acids precipitated on acidification adsorbing tannin with formation of the coloured complexes. If the alkali-salt solutions are treated first with mineral acid, then with tannin, the white earth-acid precipitates first formed assume the characteristic colour of the tannin precipitates ; in this case, however, the adsorption of tannin is more superficial, and hence the colorations are less intense.

According to Rose, the tannin reaction is inhibited by oxalic, tartaric, or citric acid. Whilst this holds good for the free organic acids at fairly high concentrations, we have proved that quantitative precipitation of the earth acids as tannin complexes is readily achieved by appropriate treatment of the neutralised solutions.

Extraction of a pyrosulphate melt of the pentoxides with dilute sulphuric acid containing tannin yields a coloured, compact residue of the earth-acid tannin complexes. In this connection we must discuss one of the great obstacles in the path of the earlier investigators. Titania is rendered soluble in dilute sulphuric acid after a bisulphate fusion, whereas the earth acids remain insoluble under those conditions. Hence the treatment was at first held to separate titania from the earth acids ; subsequently, however, it was recognised that association causes a profound alteration in the specific properties of the pure oxides. If the earth acids preponderate over titania, a large proportion of titania remains in the insoluble residue, but the solution contains earth acid as well as titania. If the reverse is the case, the pyrosulphate melt may dissolve in the cold to a perfectly clear liquid. This "loss of individuality"¹ is explained by the formation of complex precipitates and peptisation.

Now we have shown that addition of tannin to the dilute sulphuric acid used for leaching the pyrosulphate melt of the mixed oxides restores their individuality, the small particles of the molecularly dispersed sulphates of potassium and titanium (and other metals, *e.g.*, zirconium, uranium, if present) diffusing into the tannin sol ; whereas the larger earth-acid aggregates are entangled and coagulated by it as soon as they are formed by the disintegration of the melt.²

The formation of insoluble tannin adsorption complexes is a common property of metallic elements in general and of the earths in particular. We have proved that the precipitation is not prevented by organic acids, hence the latter need not be

¹ Crookes, *loc. cit.* (Chapter I, p. 2).

² The above procedure (the "pyrosulphate-tannin method") is used by us in the separation of titania from the earth acids (§ 54).

SALICYLIC COMPLEXES

removed prior to recovery of the elements from the solution. Just as hydrogen and ammonium sulphides are used as precipitants for sulphide-forming metals from solutions containing tartaric acid, so tannin can be employed as a general reagent for the precipitation from tartrate solution of the elements that are not precipitated as sulphides. The tannin complexes are voluminous, flocculent precipitates, several of which are strongly coloured :

<i>Group A.</i>	<i>Group B.</i>	<i>Group C.</i>
W : brown.	Zr : colourless.	Ce : darkens on exposure.
Ta : yellow.	Th : colourless.	Other rare earths : colourless.
Nb : red.	Al : colourless.	Be : colourless.
Ti : red.	Fe : blue-black.	Mn : darkens on exposure.
V : dark-blue.	Cr : greenish.	
	U : brown.	

The above classification of the tannin complexes into three groups according to their solubility in acids is based upon the results of our researches (§ 75). The following properties of the precipitates are of practical interest :

Group A precipitates. W, Ta, Nb : insoluble in mineral acids.

Ti : soluble in mineral acids.

Ta, Nb, Ti : insoluble in weakly acid oxalate solution half saturated with ammonium chloride ; insoluble in nearly neutral tartrate solution containing ammonium acetate.

W : not precipitated by itself from solutions containing organic acids, but partial precipitation induced by other tannin complexes of group A.

Group B precipitates. Soluble in weakly acid oxalate solution half saturated with ammonium chloride, insoluble in ammoniacal oxalate solution. Insoluble in nearly neutral tartrate solution containing ammonium acetate.

Group C precipitates. Soluble in nearly neutral tartrate solution containing ammonium acetate. Insoluble in ammoniacal tartrate solution, the cerium and manganese precipitates darkening on exposure to the air.

10. The Salicylic Complexes

These compounds are analytically important because their comparative insolubility permits the separation of the earth acids from titania, which forms a stable, soluble salicylic complex (§ 55). The earth-acid compounds are fairly bulky precipitates : the tantalum compound is white, the niobium compound yellow. They are soluble in oxalic acid. The titanium complex forms

PER-ACIDS

orange-coloured crystals which dissolve in dilute alkali salicylate solution to a clear, yellow to deep orange liquid ; its colour is the same as that of a solution of pertitanic acid.

11. The Per-Acids

The pyrosulphate melt of the pentoxides is soluble in a mixture of hydrogen peroxide and dilute sulphuric acid, forming a colourless solution of pertantallic and perniobic acids. An important analytical application of the per-acids is based on the fact that their solution is colourless whilst pertitanic acid forms a strongly coloured solution. It is therefore possible colorimetrically to determine small amounts of titania in the pentoxides without an actual separation. Perniobic acid is more stable than the tantalum compound ; the solution of the latter gets cloudy on standing, and later deposits a precipitate. According to Hahn and Gille,¹ the solution of the per-acids is more or less colloidal. We obtain a clear solution of the per-acids by dissolving the pyrosulphate melt of the mixed oxides in ammonium oxalate solution and treating it with sulphuric acid and hydrogen peroxide.

¹ *Z. anorg. Chem.*, 1920, 112, 283.

CHAPTER III

THE CHEMICAL COMPOSITION OF TANTALUM AND NIOBIUM MINERALS

THIS chapter presents a brief survey of the better-known earth-acid minerals, with representative complete analyses taken from the mineralogical literature. Crystallographic, physical, and other data are not discussed, the inclusion of a mineralogical chapter in this analytical laboratory manual being considered useful chiefly for the sake of the qualitative and approximate quantitative data furnished by the analyses. Owing to the imperfection of the methods hitherto available, the reliability of the quantitative data so far published is necessarily doubtful, and remains to be confirmed or disproved by future investigations, of which this volume is intended to form the first step. As it is, the constitution and relationship of the more complex earth-acid minerals are by no means clear, and their number has been increased, perhaps unnecessarily, by the inclusion of newly named, ill-defined species. In the opinion of Hillebrand and Lundell,¹ "many of the formulæ that have been assigned are purely hypothetical, being based on unproved and in part probably unprovable assumptions. . . . There is no other class of minerals of which the analysis is so beset with difficulties. . . . Doubtless many analyses and formulæ reported are worthless quantitatively and defective qualitatively . . ."

In assembling the data for this chapter I have largely consulted Doelter's *Handbuch der Mineralchemie*,² in which the monographs on the minerals cited have been compiled by G. T. Prior, F. Zambonini and H. Leitmeier.

In mineralogical text-books, earth-acid minerals are usually classified according to crystallographic characters. The following list is given by E. S. Dana :³

- (1) *Pyrochlore group* ; isometric. Pyrochlore, koppite, hatchet-tolite, microlite.
- (2) *Fergusonite group* ; tetragonal. Fergusonite, sipylite.
- (3) *Columbite group* ; orthorhombic. Columbite, tantalite, skogbölite. Tetragonal Tapiolite.
- (4) *Samarските group* ; orthorhombic. Yttrotantalite, samarskite, annerödite, hielmite.

¹ *Op. cit.*, p. 464.

² Vol. III, Part I (1918).

³ *System of Mineralogy*, 6th Edition, New York, p. 723.

TANTALONILOBATE MINERALS

(5) *Aeschynite group* ; orthorhombic. Aeschynite, polymignite, euxenite, polycrase.

The grouping adopted in this chapter is based upon chemical composition, an arrangement of more immediate practical interest to the worker engaged in the analysis of the minerals. Those in which tantalum and niobium occur as essential constituents are here classified in two groups, namely the tantaloniobates and the titanoniobates. A third group has been formed of minerals that contain tantalum and niobium in subordinate, though sometimes fairly substantial amounts, the preponderating constituent being an oxide of the type $R''O_2$ ($R = Ti, Zr, Sn$).

GROUP I. TANTALONILOBATES

These are compounds of tantalic and niobic acids with various metallic oxides, and free from, or poor in, titania.

Columbite-tantalite. Orthorhombic iron manganese tantaloniobate, $(Fe, Mn)O \cdot (Nb, Ta)_2O_5$. The term tantalite is applied to the tantalum-rich members of the isomorphous series ; the prefixes *manganite* and *ferro* may be used to denote the preponderance of either protoxide. (Analyses Nos. 1-7.)

The specific gravity increases with the tantalum content. Simpson's table,¹ reproduced below, shows the relation between the specific gravity and the percentage of tantalic oxide (within about 5 per cent.) in the mineral.

Specific gravity.	Per cent. Ta_2O_5	
	Ferrotantalite.	Manganotantalite.
5·3	trace.	2
5·5	6	10
5·7	14	19
5·9	22	27
6·1	30	36
6·3	38	44
6·5	45	51
6·7	52	59
6·9	59	66
7·1	65	72
7·3	70	78
7·5	75	83
7·7	79	—
7·9	84	—

¹ *West. Austral. Geol. Survey, Bull. 23, 1906, p. 72.*

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Columbite.				Tantalite.				
No. Sp. Gr.	1 5'395	2 5'75	3 5'780	No. Sp. Gr.	4 7'301	5 6'750	6 7'03	7 7'74
MgO	0.23	0.40	—	MgO	—	—	0.15	0.19
CaO	trace	—	—	CaO	0.17	—	trace	—
MnO	3.28	2.39	7.51	MnO	13.88	10.40	14.15	3.78
FeO	17.33	15.82	12.64	FeO	1.17	6.11	1.63	10.89
PbO	0.12	—	—	NiO	—	—	trace	0.02
SnO ₂	0.73	0.58	0.09	SnO ₂	0.67	0.13	0.48	1.51
ZrO ₂	0.13	0.28	—	WO ₃		—	trace	0.13
WO ₃	0.13	1.07	—	TiO ₂		—	0.40	0.71
Nb ₂ O ₅	77.97	56.43	60.52	Nb ₂ O ₅	4.47	29.78	15.11	2.50
Ta ₂ O ₅	—	22.79	19.71	Ta ₂ O ₅	79.81	53.28	68.65	80.61
H ₂ O	—	0.35	—	H ₂ O	0.16	—	0.07	0.14
	99.92	100.11	100.47		100.33	99.70	100.64	100.48

No. 1 : Groenland (Anal. Blomstrand, *J. prakt. Chem.*, 1866, 99, 44). This analysis represents the mineral as being free from tantalum. Prior to the discovery of the tannin separation method, small amounts of tantalum could not be determined in presence of much niobium. A fresh analysis, involving fractional precipitation of the earth-acid fraction by tannin, would be interesting.

No. 2 : Bodenmais (Anal. Blomstrand, *loc. cit.*). No. 3 : Haddam, Conn. (Anal. Headden, *Amer. Journ.*, 1891, 41, 89). No. 4 : Sanarka, Ural (Anal. Blomstrand ; Arzruni, *Verh. d. kais. russ. min. Ges.*, 1887, 23, 188). No. 5 : Black Hills, S. Dakota (Anal. Headden, *loc. cit.*). No. 6 : Wodgina, W. Australia (Anal. Simpson, *Austr. Assoc. Adv. Sci.*, 1907, 11, 449). No. 7 : Greenbushes, W. Austr. (Anal. Simpson, *loc. cit.*).

Tapiolite (Analyses Nos. 8, 9). Tetragonal iron manganese tantaloniobate. Similar analyses have been published for skogbölite, ixiolite and mosite.

Stibiotantalite (Analyses Nos. 10, 11). Orthorhombic antimony tantaloniobate, Sb₂O₃. (Ta, Nb)₂O₅.

Tapiolite.			Stibiotantalite.			Bismutotantalite.	
No. Sp. gr.	8 7.496	9 7.22	No. Sp. gr.	10 7.37	11 —	No. Sp. gr.	12 8.44
MnO	0.81	—	NiO	0.08	—	MnO	0.12
FeO	14.47	16.85	Fe ₂ O ₃	trace	—	(Fe, Al) ₂ O ₃	0.11
WO ₃	—	0.11	Bi ₂ O ₃	0.82	0.60	Bi ₂ O ₃	52.26
SnO ₂	0.48	0.38	Sb ₂ O ₃	40.23	40.95	Zr, Ti	trace
TiO ₂	—	trace	Nb ₂ O ₅	7.56	16.19	SnO ₂ + Sb ₂ O ₃	0.04
Nb ₂ O ₅	11.22	4.29	Ta ₂ O ₅	51.13	41.92	Nb ₂ O ₅	6.63
Ta ₂ O ₅	73.91	78.61	H ₂ O	0.08	—	Ta ₂ O ₅	40.12
	100.89	100.24		99.90	99.66	Ignition loss	0.33
							99.61

No. 8 : Sukula, Finland (anal. Rammelsberg, *Sitzungsber. Berliner Akad.*, 1871, 181). No. 9 : Custer City, S. Dakota (anal. Headden, *Proc. Colo. Sci. Soc.*, 1906, 8, 167). No. 10 : Greenbushes, W. Australia (anal. Goyder, *Chem. Soc. Trans.*, 1893, 1076). No. 11 : anal. Foote and Langley, *Amer. J. Sci.*, 1910, 30, 398. No. 12 : Gamba Hill, Uganda (anal. Wynn ; Wayland and Spencer, *Min. Mag.*, 1931, 22, 185).

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Bismutotantalite (Analysis No. 12). Orthorhombic bismuth tantaloniobate, $\text{Bi}_2\text{O}_3 \cdot (\text{Ta}, \text{Nb})_2\text{O}_5$.

Microlite (Analyses No. 13, 14). Isometric. A tantaloniobate of calcium, with or without alkalis and fluorine. *Koppite* appears to have the same composition as microlite. *Hatchettolite* differs from either in containing uranium.

Samarските—*Yttrotantalite* (Analyses Nos. 15–19). Orthorhombic, isomorphous: samarskite is mainly a niobate, yttrotantalite a tantalate, of yttrium, calcium, iron and uranium. Constitution uncertain. *Nohlite*, *vietinghofite*, *loranskite* and *plumboniobite* can perhaps be classed under samarskite. *Annerödite* has been recognised as a parallel growth of columbite on samarskite. *Hielmite* may be related to yttrotantalite. *Ampangabeite* is possibly an altered samarskite.

Fergusonite (Analyses Nos. 20–24). Tetragonal. Chiefly yttrium tantaloniobate, containing uranium and lime; constitution uncertain. *Sipylite* is perhaps identical with fergusonite; *risörite* is a doubtful relative of this species.

Microlite.			Samarските.				Yttrotantalite.	
No. Sp. gr.	13 5·656	14 5·422	No. Sp. gr.	15 4·95	16 —	17 5·670	18 5·92	19 5·85
Na_2O	2·86	1·66	Na_2O	0·23	0·76	0·10	0·57	0·81
K_2O	0·29	0·20	K_2O	0·39	0·08	0·21	trace	0·10
BeO	0·34	—	BeO	—	0·30	—	0·35	0·58
MgO	1·01	0·42	MgO	0·11	0·13	0·17	0·15	0·15
CaO	11·80	13·46	CaO	5·38	4·30	2·62	1·28	2·42
MnO	—	0·60	MnO	0·51	0·86	0·67	1·85	1·01
FeO	—	3·64	FeO	4·83	4·40	3·04 ¹	7·48	7·61
Fe_2O_3	0·29	—	BaO	—	0·38	0·09 ²	—	—
Al_2O_3	0·13	—	PbO	—	0·77	0·86	—	0·30
Y earths	0·23	—	Al_2O_3	—	0·36	—	—	—
Ce earths	0·17	—	Y earths	14·34	9·07	27·54	16·06	16·06
UO_3	1·59	—	Ce earths	4·78	0·89	4·76	2·13	0·92
WO_3	0·30	—	SnO_2	0·10	0·57	0·04	1·20	2·96
SnO_2	1·05	—	ZrO_2	—	0·62	0·02	0·57	0·46
TiO_2	—	0·90	ThO_2	—	2·51	1·55	0·67	0·81
Nb_2O_5	7·74	3·62	UO_2	—	0·66	6·14	3·85	4·48
Ta_2O_5	68·43	73·54	UO_3	10·75	6·78	2·08	—	—
F	2·85	—	WO_3	—	—	0·02	0·66	2·02
H_2O	1·17	1·28	SiO_2	—	1·82	—	0·96	0·61
			TiO_2	—	—	2·20	1·67	2·63
			Nb_2O_5	55·41	38·83	41·00	20·38	17·75
			Ta_2O_5	—	10·70	4·62	39·53	37·26
			H_2O	2·21	6·54	1·31	0·51	1·16
				99·04	100·33	99·14	99·87	100·10

¹ Fe_2O_3 .

² ZnO .

TITANONIOBATE MINERALS

No. 13 : Amelia Court House, Virg. (anal. Dunnington, *Amer. Journ.*, 1881, 23, 130). No. 14 : Wodgina, W. Australia (anal. Simpson, *Austral. Assoc. Adv. Sci.*, 1909, 12, 310). No. 15 : Berthier Co., Quebec (anal. Hoffmann, *Amer. Journ.*, 1882, 24, 475). No. 16 : Ödegårdsletten, Norway (anal. Blomstrand ; Brögger, *Die Minerale der südnorwegischen Granit u. Pegmatitgänge*, 1906, 142). No. 17 : Petaca, N. M. (anal. Wells, *J. Amer. Chem. Soc.*, 1928, 50, 1017). No. 18 : Berg, Norway (anal. Blomstrand ; Brögger, *loc. cit.*, 154). No. 19 : Hattevik (as for No. 18).

Fergusonite.						Æschynite.		
No. Sp. gr.	20 4·751	21 5·267	22 5·023	23 5·58	24 6·236	No. Sp. gr.	25 5·230	26 5·142
MgO	—	—	—	0·37	—	CaO	2·75	2·50
CaO	3·04	2·21	2·02	1·40	2·18	FeO	3·17	4·24
MnO	—	—	—	—	0·87	Al ₂ O ₃	—	trace
FeO	0·60	—	—	0·59	trace	Y earths	1·12	4·59
Fe ₂ O ₃	—	—	0·51	—	—	Ce earths	24·09	19·58
Y earths	38·04	36·63	37·91	31·20	31·38	SiO ₂	—	trace
Ce earths	1·79	3·33	—	6·15	0·94	TiO ₂	21·81	22·51
TiO ₂	—	—	—	—	2·20	SnO ₂	0·18	trace
SnO ₂	0·23	0·83	—	0·20	—	ThO ₂	15·75	15·52
ThO ₂	—	—	—	2·07	1·02	Nb ₂ O ₅	29·64	23·74
UO ₃	1·20	8·16	5·11	6·15	1·18	Ta ₂ O ₅	—	6·91
Nb ₂ O ₅	39·93	43·36	44·65	50·10	2·15	Ign. loss	1·07	—
Ta ₂ O ₅	9·53	2·04	4·98	—	55·51			
WO ₃	0·21	—	—	—	—			
H ₂ O	5·20	4·18	4·58	1·94	3·36			
	99·77	100·74	99·76	100·17	100·79		99·58	99·59

No. 20 : Groenland (anal. Rammelsberg, *Bel. Ak.* 1871, 406). No. 21 : Helle, Norway (as for No. 20). No. 22 : Rakwana, Ceylon (anal. Prior, *Min. Mag.*, 1893, 10, 234). No. 23 : Madagascar (anal. Pisani ; Lacroix, *Bull. Soc. Min.*, 1908, 31, 312). No. 24 : Cooglegong, W. Austr. (anal. Simpson, *Austral. Assoc. Adv. Sci.*, 1909, 12, 310). No. 25 : Miask, Ural (anal. Marignac, *Bibl. Univ.*, 1867, 29, 282). No. 26 : Hitterö, Norway (anal. Tschernik, *Bull. Akad. Sci. St. Petersburg*, 1908, 389).

GROUP II. TITANONIOBATES

These minerals contain titania in addition to earth acid as essential constituents. Nearly all are characterised by a high rare-earth content.

Æschynite (Analyses Nos. 25, 26). Orthorhombic. A titanoniobate of cerium metals, thoria, lime and iron, of uncertain composition.

Euxenite—*Polycrase* (Analyses Nos. 27–32). Orthorhombic, isomorphous. Titanoniobates of yttria earths and uranium, with lime and ferrous oxide, of uncertain composition.

TITANONIOBATE MINERALS

Two other minerals, *priorite* and *blomstrandine*, both orthorhombic, do not differ materially from euxenite in chemical composition. The above four minerals exhibit interesting crystallographic affinities, which remain to be more clearly related to their constitution.

Pyrochlore (Analyses Nos. 33–35). Isometric. A titanoniobate of lime, ceria earths and soda, containing fluorine. Constitution doubtful.

Blomstrandite, *betafite* and *samiresite* are octahedral titanoniobates differing from pyrochlore in containing no alkali or fluorine, but much uranium. *Marignacite* is regarded as a variety of pyrochlore containing silica, but no fluorine.

No. Sp. gr.	27 5·37	28 —	29 4·79	30 —	31 4·996	32 5·00
MgO	0·35	0·08	0·25	—	0·22	0·28
CaO	1·02	0·85	1·90	—	4·12	1·04
FeO	trace	1·37	2·25	2·04	5·63	1·73
PbO	—	0·43	—	0·96	—	0·35
MnO	0·34	—	—	—	0·19	0·16
Al ₂ O ₃	0·76	trace	1·65	—	—	1·36
Ce earths	3·55	2·45	2·20	6·93	4·32	4·69
Y earths	23·03	27·32	17·80	22·01	17·11	26·66
SiO ₂	—	—	—	—	2·12	—
TiO ₂	30·43	24·43	23·10	17·45	21·89	34·07
ZrO ₂	—	—	—	—	—	0·50
SnO ₂	—	0·11	—	0·07	0·29	0·20
ThO ₂	1·76	4·60	2·80	2·04	0·61	7·93
UO ₂	6·69 ¹	5·64	14·70	7·91	0·49	3·24
WO ₃	—	trace	—	0·11	—	trace
UO ₃	—	—	—	—	2·14	—
Nb ₂ O ₅	4·35	29·00	29·30	28·20	36·68	15·08
Ta ₂ O ₅	23·10	1·01	3·95	9·35	—	1·30
H ₂ O	2·82	2·87	—	2·21	3·69	0·96
	100·20	100·16	99·90	99·28	99·50	99·55

No. 27 : Euxenite, Cooglegong, W. Australia (anal. Simpson, *Austr. Assoc. Rep.*, 1909, 310). No. 28 : Euxenite, Eitland, Norway (anal. Hauser and Wirth. *Ber.* 1909, 42, 4443). No. 29 : Euxenite, Samiresy, Madagascar (anal. Pisani ; Lacroix, *Bull. Soc. Min.*, 1912, 35, 91). No. 30 : Polycrase, S. Carolina (anal. Hauser and Wirth, *loc. cit.*). No. 31 : Priorite, Embabaan, Swaziland (anal. Prior, *Min. Mag.* 1899, 12, 97). No. 32 : Blomstrandine, Miask, Ural (anal. Hauser and Herzfeld, *Zentr. Blatt Mineral.*, 1910, 756).

Epistolite (Analysis No. 36). Monoclinic. A very rare mineral containing silicate, titanate and niobate of sodium. Only one analysis has so far been made.

¹ U₂O₃.

OTHER MINERALS

Wiikite (Analysis No. 37). Orthorhombic. Of great interest as a scandium mineral. Its constitution is as yet unknown.

Loranskite appears to be allied to wiikite, but contains more yttrium and less uranium.

No. Sp. gr.	33 4·353	34 4·955	35 4·13	36 2·885		37 4·85
Na ₂ O	3·44	2·35	2·52	17·59		
K ₂ O	1·41	—	0·57	trace		
MgO	—	trace	0·16	0·13		
CaO	16·75	10·62	4·10	0·77		
FeO	4·20	—	0·52 ¹	0·20	Fe ₂ O ₃	15·52
Ce earths	3·99	5·90	13·33	0·30 ²	Sc ₂ O ₃	1·17
Y earths	—	0·46	5·07	—	Y earths	7·64
SiO ₂	—	—	3·10	27·59	Ce earths	2·55
ZrO ₂	2·90	4·65	—	—	SiO ₂	16·98
ThO ₂	0·41	trace	0·20	—	ThO ₂	5·51
TiO ₂	3·70	9·11	2·88	7·22	(Ti, Zr)O ₂	23·36
Nb ₂ O ₅	58·83	30·70	55·22	33·56	UO ₃	3·56
Ta ₂ O ₅	—	33·03	5·86	—	M ₂ O ₃	15·91
F	4·34	2·17	—	1·98	Ign. loss	5·83
H ₂ O	0·78	1·37	6·40	11·01		98·03
—O—F ₂	100·75 1·83	100·36 0·91	99·93	100·35 0·83		
	98·92	99·45		99·52		

No. 33: Alnö (anal. Holmquist, *Geol. För. Förh.*, 1893, 15, 588). No. 34: Sundsvall, Sweden (anal. Tschernik, *Journ. phys. chim. Russe*, 1904, 36, 712). No. 35: Wisconsin (anal. Weidman and Lehner, *Amer. Journ.* 1907, 23, 287). No. 36: Julianehaab, Groenland (anal. Christensen, *Meddel. om Grönland*, 1900, 24, 188). No. 37: Impilako, Finland (anal. Crookes, *Z. anorg. Chem.*, 1909, 61, 349).

GROUP III. OTHER MINERALS CONTAINING EARTH ACID

(a) *Minerals in which Titania preponderates.* *Strüverite*—*Ilmenorutile* (Analyses Nos. 38–41). Tetragonal, isomorphous. Minerals of uncertain constitution, closely related to rutile in crystal structure and containing titania with ferrous tantalate and niobate; strüverite is richer in tantalite, ilmenorutile richer in niobite, oxide.

Dysanalyte (Analysis No. 42). Isometric. A titanate of calcium containing niobite oxide.

¹ Fe₂O₃. Mn, Sn, W: traces.
² MnO.

OTHER MINERALS

No. Sp. gr.	38 —	39 5·14	40 5·59	41 5·25		42 4·21
MgO	0·04	—	0·17	—	Na ₂ O	4·37
CaO	0·22	trace	0·51	—	CaO	25·60
MnO	trace	—	trace	—	MnO	0·23
FeO	11·58	10·56	11·15	7·3	FeO	9·22
SiO ₂	0·23	—	—	2·0	Ce ₂ O ₃	2·80
TiO ₂	73·78	53·04	41·09	47·8	SiO ₂	2·21
SnO ₂	—	—	—	1·3	TiO ₂	50·93
Nb ₂ O ₅	13·74	21·73	23·47	6·2	Nb ₂ O ₅	4·86
Ta ₂ O ₆	0·43	14·70	23·47	34·8		
H ₂ O	—	—	—	0·4		
	100·02	100·03	99·86	99·8		100·22

No. 38 : Evje, Norway (anal. Heidenreich ; Brögger, *Minerale südnorweg. Granit u. Pegmatitgänge*). No. 39 : Ilmen Mountains (anal. Prior, *Min. Mag.*, 1908, 15, 87). No. 40 : Craveggia, N. Piedmont (anal. Prior, *Min. Mag.*, 1908, 15, 84). No. 41 : Black Hills, S. D. (anal. Wells, *Amer. J. Sci.*, 1911, 31, 440). No. 42 : Vogtsburg (anal. Hauser, *Z. anorg. Chem.*, 1908, 60, 237).

(b) *Minerals in which Zirconia preponderates.* *Naegite* and *Hagatalite* (Analyses Nos. 43, 44), appear to be closely related to zircon ; their constitution is uncertain. By some investigators they are regarded as varieties of zircon, whilst others look upon them as isomorphous mixtures of dioxides. *Azorite* is a variety of zircon said to contain niobium.

No. Sp. gr.	43 4·4	44 4·4	45	46 2·85-3·0	47 2·9-3·1	48		49 4·77-4·85
Na ₂ O	—	—	10·77	14·18	11·17	7·50	K ₂ O	0·77
K ₂ O	—	—	—	—	0·11	—	Na ₂ O	0·59
MgO	—	0·2	—	—	—	0·12	MgO	0·16
CaO	—	0·3	9·70	9·12	12·11	26·95	CaO	6·98
MnO	—	—	5·59	2·74	3·60	1·00	MnO	1·32
FeO	—	—	—	6·70	3·90	1·26	FeO	2·08
Fe ₂ O ₃	1·42	2·3	4·73	—	—	0·48	PbO	0·39
Al ₂ O ₃	—	2·8	—	—	—	—	Al ₂ O ₃	0·10
Y earths	—	—	—	—	0·32	—	Fe ₂ O ₃	7·66
Ce earths	6·68	13·1	—	3·05	4·80	0·66	Ce earths	11·04
SiO ₂	29·55	29·7	29·63	50·39	45·15	30·12	Y earths	2·26
TiO ₂	—	—	2·35	—	—	0·42	ThO ₂	3·92
ZrO ₂	53·03	42·0	28·79	12·40	12·51	16·11	SiO ₂	0·45
ThO ₂	2·85	1·5	—	—	—	—	TiO ₂	18·90
UO ₂	2·69	trace	—	—	—	—	ZrO ₂	29·71
Nb ₂ O ₅	—	—	—	0·41	3·52	12·85	SnO ₂	0·15
Ta ₂ O ₅	1·12	2·7	5·20	—	—	—	Nb ₂ O ₅	11·99
Cl	—	—	—	1·20	0·55	—	Ta ₂ O ₅	1·35
F	—	—	—	—	—	2·98	H ₂ O	0·28
H ₂ O	2·77	5·5	2·24	0·26	2·11	0·74		
(—O ~ F)	100·11	100·1	99·00	100·54	99·85	101·19 1·24		100·09
						99·95		

OTHER MINERALS

No. 43 : Naegite, Naegi, Japan (anal. Shibata and Kimura, *Japan. J. Chem.*, 1923, 2, 4). No. 44 : Hagatalite, Hagata, Japan (anal. Kimura, *ibid.*, 1925, 2, 83). No. 45 : Låvenite, Klein-Arö (anal. Cleve, *Z. Kryst.*, 1890, 16, 343). No. 46 : Eudialyte, Narsarsak, Groenland (anal. Christensen; Bøggild, *Mineral. groenlandica*, 1905, 495). No. 47 : Eukolite, Barkevik, Norway (anal. Cleve, *Z. Kryst.*, 1890, 16, 503). No. 48 : Wöhlerite, Langesundfjord (anal. Cleve, *ibid.*, 360). No. 49 : Polymignite, Frederiksvärn, Norway (anal. Blomstrand; Brögger, *loc. cit.*, 391).

Eudialyte, *Eukolite*, *Låvenite*, *Wöhlerite* (Analyses Nos. 45-48). These four rare minerals may be classed together as silicozirconates containing much lime and soda. The two former are trigonal, the two latter monoclinic. The constitution of all these minerals is quite doubtful.

Polymignite (Analysis No. 49), orthorhombic, is a titanozirconate of unknown constitution, which appears to be crystallographically and physically related to æschynite.

(c) *Minerals in which Tin preponderates*. *Ainalite*, *Tantalocassiterite* (Analyses Nos. 50-52). Tetragonal. Three occurrences of tantaliferous cassiterite are discussed by Schaller,¹ who suggests that the minerals are isomorphous mixtures of stannyl stannate, $\text{SnO} \cdot \text{SnO}_3$ (*i.e.*, cassiterite) and tetragonal ferrous tantalate, $\text{Fe}(\text{TaO}_3)_2$ (*i.e.*, tapiolite).

No. Sp. gr.	50		51 6·77		52 6·62
CuO	0·78			FeO	1·62
Fe ₂ O ₃	2·04	FeO	1·11	SiO ₂	1·00
SnO ₂	88·95	SnO ₂	95·18	SnO ₂	94·36
Ta ₂ O ₅	8·78	Ta ₂ O ₅	3·82	Ta ₂ O ₅	2·42
	100·55		100·11		99·40

No. 50 : Finland (anal. Nordenskiöld); No. 51 : Mecklenburg, N.C. (anal. Headden); No. 52 : Etta Mine, S. D. (anal. Headden); quoted by Schaller (*loc. cit.*).

(d) *Monazite*. A few occurrences have been described as containing a little tantallic acid, and it has been suggested that Ta_2O_5 is capable of replacing P_2O_5 isomorphously. More work appears to be necessary to decide this question; in the opinion of Johnstone,² the tantalum content is due to an admixture of tantalite or other earth-acid mineral in detrital monazite.

¹ *U.S.G.S. Bulletin*, 509, 1912.

² *J. Soc. Chem. Ind.*, 1914, 33, 55.

CHAPTER IV

ANALYTICAL TECHNIQUE

THIS chapter describes the common operations and manipulations of earth-acid analysis; the technique recommended has been gradually evolved in the course of our researches. To facilitate the use of the book, the directions for analytical procedures will be given throughout in paragraphs provided with headings and consecutive reference numbers.

The pentoxides may be brought into solution by treatment with (1) an alkaline flux, (2) an acid flux, or (3) hydrofluoric acid. In each case we will describe the process of obtaining the soluble earth-acid compound, the precipitation of the earth acids from the solution, the manipulation of the precipitates, and the quantitative determination of the recovered pentoxides:

- | | |
|----------------------------------|----------------|
| I. Alkaline fluxes | see §§ 1 to 6. |
| II. Acid flux. | „ §§ 7 to 16. |
| III. Hydrofluoric acid | „ § 17. |

I. ALKALINE FLUXES

We consider fusion with caustic alkali undesirable on account of unavoidable contamination of the melt with the material of the crucible: the only application we have made of it is for the determination of the pentoxides in tungstic oxide (§ 39). We apply potassium carbonate (§ 1) or sodium carbonate (§ 6).

§ 1. Fusion with Potassium Carbonate: Lixiviation

The pentoxides (0.1 to 0.5 g.) are fused with 3 g. of potassium carbonate in a platinum crucible over a strong burner until the fusion is clear; it is then made to solidify round the sides of the crucible. A gold crucible may be used for niobic or the mixed pentoxides; for tantalic oxide a platinum crucible is recommended as a higher temperature is required, with attendant risk of damage to a gold crucible. The fluid tantalate melt usually shows a faint mistiness comparable to the Tyndall phenomenon, but a niobate melt is quite clear.

A small fragment of potassium hydroxide (0.3 to 0.5 g.) is added to the cold crucible, and warm water until the melt is

covered. The crucible is left on a hot plate until solution is complete. The addition of potassium hydroxide prevents hydrolysis of the tantalate solution, but is really unnecessary in the case of niobic oxide ; however, we always add the potassium hydroxide so as to work under uniform conditions with mixed oxides.

The clear solution is transferred to a 250-ml. beaker with a minimum of hot water.

§ 2. Precipitation of the Sodium Salts

The hot solution of the potassium salts obtained as in § 1 is gradually treated with an excess of solid sodium chloride (about 17 g. for 50 ml. of solution), the beaker being rotated while the salt is added. The sides of the beaker are rinsed down with a little half-saturated sodium chloride solution. After standing in the cold overnight, the pulverulent precipitate is collected on a 7- or 9-cm. paper and well washed with half-saturated sodium chloride solution, by decantation first until the excess of solid sodium chloride has dissolved. The filter and precipitate are returned to the precipitation beaker. (Further treatment : § 4.)

The presence of potassium hydroxide ensures not only the easier solution of a tantalate melt, but also the more satisfactory precipitation of sodium tantalate. The precipitation of the earth acids is never quite complete, a few mg. passing into the filtrate by virtue of the solubility of the sodium salts (see § 3).

§ 3. Bicarbonate Hydrolysis

The small amount of earth acid remaining in solution after precipitation with sodium chloride (§ 2) is recovered as follows : the filtrate is treated with phenolphthalein, just decolorised with *N* hydrochloric acid, and digested on the water-bath. When the pink colour returns, it is again discharged by further addition of a little acid, followed by further heating. Digestion on the water-bath with occasional neutralisation is continued for two to three hours, after which time the colour of the indicator is almost completely and permanently discharged and the small precipitate has flocculated. It is collected on a small paper containing a little filter pulp, and washed with half-saturated sodium chloride solution. (Further treatment : § 4.)

§ 4. Gravimetric Determination of the Pentoxides after Potassium Carbonate Fusion

The small hydrolysis precipitate (§ 3) is added to the precipitated sodium salt (§ 2). The filters are pulped by means of a

glass rod in 50 ml. of hot water ; the solution is slightly acidified with *N* hydrochloric acid, and digested on the water-bath for half an hour. It is then neutralised with ammonia to methyl orange, and again digested hot for about an hour. The precipitate is collected, washed with 2 per cent. ammonium nitrate solution for the removal of the sodium salt, and the wet filter and content are heated in a tared porcelain crucible on an asbestos mat until the paper is charred. After the disappearance of the organic matter the ignition is concluded by ten minutes' heating over a good burner. The precipitate is weighed as $(\text{Ta}, \text{Nb})_2\text{O}_5$.

Constant weight is rapidly attained in this and other ignitions, especially of tannin precipitates. This is due to the fine state of division of the precipitate left after the destruction of the organic matter (cellulose or tannin), and to the high temperature reached in the combustion of the carbon in intimate contact with the pentoxide or other earth.

§ 5. Approximate Simultaneous Volumetric Determination of Tantalum and Niobium

The acid required for the decomposition of sodium tantalate and niobate is proportional to the alkali, hence to the pentoxide, in the precipitate. The volumetric determination of the alkali is a simple operation, though the endpoint is not very sharp, for reasons given below. The sodium salt precipitate (§ 2), after careful washing with half-saturated sodium chloride solution for the removal of potassium carbonate and hydroxide, is returned to the beaker with the filter, which is thoroughly pulped with 50 ml. of hot water. After addition of a drop of methyl orange indicator, 0.1*N* hydrochloric acid is run into the cloudy suspension, which is kept stirred, until a permanent colour change occurs. The reading must be taken at the neutral point.

The next step in the determination is to ascertain the amount of earth acid in the titrated liquid ; since a few mg. escaped in the precipitation of the sodium salt (§ 3), it is the amount of pentoxide combined with the alkali that must be determined. The titrated liquid is treated with a slight excess of acid, followed by ammonia, the determination being carried out as in §§ 2 and 4 ; the bicarbonate precipitate (§ 3) is recovered separately.

The calculation is based upon the following data. One g. of Nb_2O_5 in the form of 7 : 6 sodium niobate neutralises 87.66 ml. of 0.1*N* acid ; one g. of Ta_2O_5 as 4 : 3 sodium tantalate neutralises 60.20 ml. Hence 87.66 ml. are equivalent to 100 per cent.

VOLUMETRIC DETERMINATION

§ 5

Nb₂O₅, whilst 60.20 ml. indicate absence of Nb₂O₅; therefore, each 1 ml. over 60.20 represents $\frac{100}{87.66-60.20} = 3.64$ per cent.

Nb₂O₅. The formula given below is used for calculating the weight of Nb₂O₅ present in the mixed oxides :

Let A = M₂O₅ taken,

B = M₂O₅ recovered after titration,

N = ml. 0.1N HCl consumed ;

Then $\left(\frac{N}{B} - 60.20\right) 0.0364A = \text{g. Nb}_2\text{O}_5 \text{ in A.}$

The figures in the table give an idea of the degree of accuracy attainable by this rapid procedure. All the determinations (with the exception of Nos. 9 and 10) were made on quantities not known to the operator until he had completed the work. Of the six simultaneous determinations (17 to 22), five gave a positive niobium error, perhaps due to retention of alkali by the filter paper. This error could be minimised by the use of a small pad of filter pulp instead of a paper, but the operation is subject to other uncertain factors, such as possible formation of mixed

Exp. No.	G. taken.	ml. 0.1N Acid.	M ₂ O ₅ found after Titration.	M ₂ O ₅ not precipitated by NaCl.	Ratio g. M ₂ O ₅ per ml.	Deviation of Ratio from Mean.
	Ta ₂ O ₅					
1	0.1558	9.15	0.1530	0.0028	0.01673	+ 0.00015
2	0.2034	12.20	0.1996	0.0038	0.01636	- 0.00022
3	0.1540	9.15	0.1516	0.0024	0.01657	- 0.00001
4	0.1621	9.63	0.1590	0.0031	0.01650	- 0.00008
5	0.2050	12.38	0.2017	0.0033	0.01629	- 0.00029
6	0.3028	17.93	0.2987	0.0041	0.01666	+ 0.00008
7	0.2024	11.83	0.1996	0.0028	0.01687	+ 0.00029
8	0.3053	17.99	0.3003	0.0050	0.01669	+ 0.00011
			Mean ratio : ¹		0.01658	
	Nb ₂ O ₅					
9	0.3010	26.77	0.2973	0.0037	0.01111	- 0.00024
10	0.2482	21.59	0.2450	0.0032	0.01135	0.0000
11	0.2666	23.17	0.2598	0.0068	0.01121	- 0.00014
12	0.3250	28.42	0.3230	0.0020	0.01137	+ 0.00002
13	0.2564	21.71	0.2508	0.0056	0.01155	+ 0.0002
14	0.2528	21.47	0.2479	0.0049	0.01155	+ 0.0002
15	0.2048	17.75	0.1976	0.0072	0.01113	- 0.00022
16	0.1814	15.06	0.1740	0.0074	0.01155	+ 0.0002
			Mean ratio : ²		0.01135	

¹ Calculated for 4Na₂O . 3Ta₂O₅ : 0.01661.

² Calculated for 7Na₂O . 6Nb₂O₅ : 0.01141.

Exp. No.	G. taken.	ml. 0.1N Acid.	M_2O_5 found after Titration.	M_2O_5 not Precipitated by NaCl.	Found.	Error, g.
17	Ta_2O_5 0.2816				0.2865	+ 0.0049
	Nb_2O_5 0.2300				0.2251	- 0.0049
18	0.5116	36.53	0.5054	0.0062	0.5116	
	Ta_2O_5 0.2132				0.2015	- 0.0117
	Nb_2O_5 0.3102				0.3219	+ 0.0117
19	0.5234	39.95	0.5182	0.0052	0.5234	
	Ta_2O_5 0.3510				0.3433	- 0.0077
	Nb_2O_5 0.1230				0.1307	+ 0.0077
20	0.4740	31.65	0.4670	0.0070	0.4740	
	Ta_2O_5 0.1752				0.1725	- 0.0027
	Nb_2O_5 0.3220				0.3247	+ 0.0027
21	0.4972	38.12	0.4879	0.0093	0.4972	
	Ta_2O_5 0.2822				0.2708	- 0.0114
	Nb_2O_5 0.1742				0.1856	+ 0.0114
22	0.4564	32.20	0.4512	0.0052	0.4564	
	Ta_2O_5 0.1952				0.1864	- 0.0088
	Nb_2O_5 0.2747				0.2835	+ 0.0088
	0.4699	35.62	0.4640	0.0059	0.4699	

crystals and the indistinct endpoint. Not only is methyl orange comparatively indifferent to 0.1N acid, but the endpoint is further obscured by the amorphous precipitate, which adsorbs acid or alkali; hence the uncertain interval between alkalinity and acidity extends over something less than 0.5 ml. The differential factor is a high one; if a stronger acid is used the factor will be higher still. No other indicators were found to be of use in the titration; we observed a marked disturbance in their normal behaviour, due no doubt to adsorption phenomena by the amphoteric gel. Cochineal forms a purple lake.

Roughly speaking, the determination is subject to an error of the order of 2 per cent., negative for Ta_2O_5 and positive for Nb_2O_5 , rather than the reverse. It was not my original intention to publish this process;¹ but seeing that it is simple and rapid, I recommend it as a guide to those not too familiar with the tannin fractionation process: the oxides recovered from the titration are

¹ *Analyst*, 1926, 51, 619 (Section VI.).

combined with the bicarbonate precipitate, and submitted to the gravimetric process (§ 61).

§ 6. Fusion with Sodium Carbonate

The pentoxides (0.1 to 0.5 g.) are fused with 3 g. (or more) of sodium carbonate in a platinum crucible until the fluid mass is clear ; this requires more prolonged heating than the fusion with potassium carbonate.

The object of the potassium carbonate fusion is to obtain the pentoxides in a water-soluble form ; sodium carbonate fusion converts them into sodium salts which remain practically insoluble when the fused mass is extracted with a solution of high sodium ion concentration.

The platinum crucible containing the sodium carbonate melt (thin layer) is placed in a nickel dish containing 50 ml. of 20 per cent. sodium hydroxide solution. When everything adhering to the crucible has been detached (a platinum rod should be used), the crucible is washed with 50 ml. of half-saturated sodium chloride solution and discarded. The liquid is allowed to stand overnight, filtered, and the residue washed with the sodium chloride solution.

The filtrate is neutralised to the bicarbonate stage and digested hot, etc., exactly as in § 3, when a very small additional precipitate of earth acid is deposited. This is added to the insoluble residue from the sodium carbonate fusion ; the filters are pulped with water, the mass acidified with hydrochloric acid, made slightly ammoniacal, etc., for the gravimetric determination of the pentoxides as described in § 4.

II. ACID FLUX

The only acid flux we apply in our operations is potassium bi- or pyrosulphate. This is far more convenient and effective than the sodium salt, which loses sulphur trioxide and solidifies at a lower temperature. Potassium bifluoride is not applied in the processes described in this book.

§ 7. Fusion with Potassium Bisulphate

A platinum crucible should not be used for this operation, for two reasons. First, the fusion is a protracted one, because any attempt to hasten it by increasing the heat results in considerable foaming, with dissipation of sulphur trioxide and risk of loss. Secondly, the fused mass becomes contaminated with platinum,

§ 7 LIXIVIATION OF BISULPHATE MELT

which interferes in subsequent operations. A silica glass or vitreosil crucible is free from these objections. In contact with the non-metallic surface, the bisulphate does not foam at all readily when rapidly heated to the dissociation temperature; hence the fusion can generally be accomplished in less than ten minutes, the crucible being manipulated with the tongs throughout.

If the flux becomes pasty before the attack is complete, it is regenerated by heating with about 0.5 ml. of strong sulphuric acid. The attack on the silica crucible is practically negligible: thus, one crucible of silica glass, which had already been in use for a long time before being put under observation, lost 0.0052 g. after thirty-two fusions, an average of 0.16 mg. per fusion.

The empty silica crucible is weighed before and after fusion; an allowance for silica can then be made, if necessary. The proportion of flux is about 3 g. for 0.25, 4 for 0.5, and 6 for 1 g. of material. The bisulphate need not necessarily be dehydrated by a preliminary fusion before the material is added: when an ignited oxide is fused for re-treatment the flux is added to it and the crucible gently heated on an asbestos mat till fused; any loss by dusting during the transfer of the oxide is thus avoided. The crucible is then held over a small free flame, gently rotated from time to time, and the heat gradually raised till the fusion is clear. The mass is made to solidify in a thin layer around the sides of the crucible; 0.5 ml. (more or less) of strong sulphuric acid is added and the fusion repeated. The mass is made to set as before.

§ 8. Lixiviation of the Bisulphate Melt with Tartaric Acid

A 10 per cent. solution of tartaric acid is convenient; the amount used should contain about the same weight of solid reagent as the bisulphate flux. When the crucible is rinsed with hot water the tartaric acid solution may become diluted to about half its strength without losing its efficiency as a solvent.

It has been found that the solution in tartaric acid of a bisulphate melt containing tantalum oxide as the only or preponderating constituent is more troublesome than that of a melt containing tantalum with a substantial admixture of other metals. No doubt solution of the tantalum is assisted by mineral associates such as niobium, titanium, zirconium, or iron. If they are absent or very subordinate, a few moments' inattention may cause a certain amount of hydrolytic precipitation of tantalum acid. As it is important for the separation of metals precipitable

as sulphides to secure a clear solution of the bisulphate fusion, the operator is advised strictly to adhere to the following directions.

The crucible is filled with hot 10 per cent. tartaric acid and allowed to stand for a short time, when the melt slides off the side of the crucible in the form of thin fragments and lumps. The contents of the crucible are stirred up and transferred to a squat 250-ml. beaker ; the crucible is well rinsed with hot water and reserved.

The liquid in the beaker is warmed and stirred without interruption until the cake and the pulverulent residue formed during its disintegration have completely dissolved and the solution is perfectly clear. If the heavy precipitate is allowed to settle during the heating, the particles begin almost at once to adhere to each other and to the bottom of the beaker ; such deposits, even if dislodged with the glass rod, are no longer completely soluble, as they leave thin translucent flakes of tantalic acid. Agitation of the liquid by continuous rotation creates an eddy at the centre of which the precipitate settles rapidly. Therefore it is necessary, in order to obtain a clear solution, to stir the liquid in all directions, preferably with a flattened glass rod, or better still, by agitation while the beaker is held at an angle of about 45° over a small bare flame. Solution of the earth acid is complete before the boiling-point is reached. The silica crucible in which the fusion was conducted is now ignited and weighed, for a silica correction if required.

If through the operator's inadvertence a little tantalic acid has separated in the form of flakes, no great harm is done as long as the solution is clear, not opalescent or cloudy. The liquid is filtered and the precipitate collected and washed with hot water ; the clear filtrate is reserved while the precipitate is ignited in silica, fused with a little bisulphate, and the melt leached with a minimum of tartaric acid ; the clear liquid is added to the reserved filtrate.

§ 9. Lixiviation with Ammoniacal Tartrate Solution

Whilst we generally use tartaric acid for the lixiviation of the bisulphate melt (§ 8), ammoniacal tartrate solution dissolves tantalic acid more readily than does tartaric acid. The melt is removed from the crucible as before by the use of the same amount of 10 per cent. tartaric acid solution containing an excess of 5 to 10 ml. of strong ammonia ; the liquid in the beaker is warmed and stirred until everything dissolves. The alkaline solution remains clear on acidification with sulphuric acid ; in fact, it often

is faintly turbid after the lixiviation, and if so a small excess of acid removes the turbidity.

§ 10. Destruction of Tartaric Acid, Tannin and Filter Paper

These substances, as well as citric and oxalic acids, etc., are destroyed by heating with sulphuric and nitric acids. That operation is not so tedious as it is reputed to be. The liquid is evaporated on a hot plate with 5 to 10 ml. (or more if no bisulphate is present) of strong sulphuric acid until it blackens and foams. Strong nitric acid is then slowly dropped into the covered beaker from a tube inserted through the spout: the black colour is discharged with copious evolution of red fumes. When this ceases the beaker is again uncovered and heated to the appearance of white fumes; if the liquid now remains colourless, all the organic matter has been destroyed; but if darkening again occurs, the treatment with nitric acid is to be repeated. During such treatment the sulphuric acid should not actually boil, but just fume. Finally, all the nitric acid is expelled by heating.

The above treatment is applied for the elimination of organic reagents when no longer required in the solution; further, it is very useful in cases where the operator, with no further material to spare, has failed to obtain a satisfactory solution of the bisulphate melt in tartaric acid. The turbid liquid is treated with sulphuric and nitric acids as described, until a clear colourless mass free from nitric acid is left; this yields a clear solution upon dilution with tartaric acid solution.

✓ § 11. Tartaric Hydrolysis

The slightly acid tartrate solution (200 to 300 ml.) is heated to boiling, stirred, and treated with 25 to 35 ml. of strong hydrochloric acid. Niobic acid is precipitated more rapidly than tantallic, but precipitation takes place in all cases within half a minute. Boiling is continued for five minutes.¹ The precipitate is allowed to settle, and filtered off; the filtration, ignition and purification of the precipitate are explained in § 13.

Nitric acid (25 to 35 ml. of the strong acid) may be used instead of hydrochloric acid for the precipitation of the earth acids by tartaric hydrolysis.

§ 12. Tannin Precipitation from Tartrate Solution

Precipitation of the earth acids with tannin may be applied either (a) to the filtrate from the hydrolysis precipitate (§ 11),

¹ Longer boiling (15 to 20 minutes), as recommended in the original directions, has been found unnecessary.

which still contains a small balance of non-precipitated pentoxides, or (*b*) to the earth-acid solution without previous tartaric hydrolysis. Procedure (*a*) is applicable to solutions containing much earth acid, with or without tungstic acid, and free or almost free from dioxide earths and uranium; whilst procedure (*b*) serves for the joint recovery of the pentoxide and dioxide earths and uranium. Tannin precipitation usually follows the removal of ferrous sulphide from ammoniacal tartrate solution.

(*a*) The combined filtrate and washings from the hydrolysis precipitate are nearly neutralised with fresh (silica-free) ammonia, boiled down to less than 150 ml., and treated with hydrogen sulphide (if necessary) for the reduction of ferric salt; the liquid is made ammoniacal, and left to settle some hours or overnight for the complete flocculation of the ferrous sulphide. The precipitate is filtered off and washed with a solution of ammonium sulphide and chloride; the filtrate is acidified with acetic acid, and boiled for the removal of hydrogen sulphide. The hot solution is made slightly ammoniacal, just re-acidified with acetic acid, treated with 5 g. of ammonium acetate and a fresh solution of 1 g. of tannin, and again boiled for a few minutes. The flocculent tannin precipitate is collected after one to two hours' standing on the water-bath (§ 13, *a*).

(*b*) The acid tartrate solution is nearly neutralised with ammonia, treated with 5 g. of ammonium acetate and 30 ml. of saturated ammonium chloride solution, and treated with hydrogen sulphide as under (*a*); it is then made ammoniacal, the ferrous sulphide being allowed to settle and removed by filtration. The filtrate (200 to 400 ml.) is re-acidified with acetic acid, boiled till hydrogen sulphide is expelled, stirred, and treated with tannin (twelve times the weight of the oxides present) in fresh 5 per cent. solution. The liquid is now left to cool and carefully titrated with ammonia (1 : 1). A strip of wet litmus paper is made to adhere to the side of the beaker so that its lower extremity is immersed in the liquid; in this manner the progress of the neutralisation can be observed in spite of the voluminous precipitate. The neutralisation should proceed to the violet colour of the indicator. The liquid is then boiled for two minutes and the precipitate left to settle and filtered off (§ 13, *b*).

§ 13. Filtration, Ignition and Purification of Tannin and Hydrolysis Precipitates

The following rules are applied in the filtration of the tannin precipitates of the pentoxide and any other earths, and of the hydrolysis precipitates of the earth acids.

(a) *Simple Filtration.* The solution (§§ 11 and 12a) is allowed to stand hot until the precipitate has settled; the clear liquid is decanted through an 11- or 12.5-cm. filter (Whatman No. 41) containing a small pad of filter pulp gently pressed into the apex. The precipitate left in the beaker is mixed with creamed filter pulp, transferred to the filter, left to drain, and returned to the precipitation vessel with a jet of wash-liquor (2 per cent. ammonium chloride for hydrolysis precipitates, or tannin precipitates from oxalate solutions; 2 per cent. ammonium chloride containing 0.5 g. of tannin per litre, for tannin precipitates produced in tartrate solutions). Precipitate and pulp are stirred into a thin cream with about 100 ml. of solution, and again collected on the filter. The washing is completed in the usual way; the last of the precipitate in the beaker is removed by rubbing a little filter pulp round the sides by means of a rubber-tipped glass rod; the beaker is thus easily and thoroughly cleaned.

(b) *Suction Filtration.* Large tannin precipitates should be filtered with the aid of gentle suction, which causes them to shrink considerably; thus, the precipitate from 0.25 g. of titania can be accommodated on two 12.5 cm. filters. A platinum or hardened paper cone and No. 40 Whatman filters (11 or 12.5 cm.) are used. The precipitates should be returned to the beaker by a stream from the wash-bottle before having become compressed and furrowed by the effect of suction. They are then churned up with wash-liquor and a little filter pulp. All the clots should be thoroughly broken up so that the precipitate may be freed from soluble salts. The suspension is returned to the filter, the beaker cleaned with filter pulp, and the washing completed.

(c) *Ignition.* None of the precipitates need be dried before ignition; they are left to drain, then transferred to a tared porcelain or silica crucible;¹ the use of the latter enables the

¹ A platinum crucible is as unnecessary for the ignition of the precipitates under discussion as it is undesirable for bisulphate fusions. When Weiss and Landecker assert that pentoxide and titania precipitates may be reduced in contact with filter paper to "blue-black" or "deep-black" oxides (*Z. anorg. Chem.*, 1909, 64, 80), we are forced to assume that their products were contaminated with undetected reducible impurities (SnO_2 , WO_3 , etc.). Whether they used platinum crucibles or not is not stated; at any rate, the permeability of platinum to reducing gases at high temperatures is an argument against its use. Having conducted thousands of ignitions of earth-acid and titania precipitates in contact with filter paper in silica and in porcelain crucibles, we can definitely state that we have never observed any perceptible discoloration to take place.

The time-honoured, tedious process of igniting hard, lumpy precipitates with addition of ammonium carbonate in platinum crucibles to constant weight is now out of date. The oxides obtained by ignition of precipitates prepared as prescribed in the text are soft, light powders which readily attain constant weight.

operator to proceed at once with a bisulphate fusion of the weighed oxide. The moist precipitate is heated on an asbestos mat until all the paper is charred. The ignition is completed on a triangle over a good Bunsen burner; the crucible is heated with the full flame for about 15 minutes after the disappearance of the carbonaceous matter. After cooling, the crucible *plus* contents is weighed as a check (the final weight is obtained later).

(d) *Leaching of the Precipitate.* The ignited and weighed oxide is cautiously transferred to a 50-ml. beaker, which is covered while a little *N* hydrochloric acid is added from a pipette. Should any oxide or filter ash adhere to the crucible, this is cleaned with the same acid, which is added to the moistened precipitate in the beaker. After half an hour's digestion on the water-bath, the liquid is made ammoniacal, the precipitate collected on a 7-cm. ashless filter, washed with 2 per cent. ammonium nitrate solution, and ignited in the same crucible on an asbestos mat, then with a strong flame for 15 minutes. The crucible is weighed, and the net weight of oxide found by subtraction of filter ash.

The lixiviation process removes small quantities of alkali and sulphur trioxide, the usual loss being of the order of 0.001 g.

(e) *Checking the Purity of the Precipitate.* In certain cases the weight of the leached precipitate may still be excessive, due to the presence of small amounts of the common impurities silica, iron or lime. A leached hydrolysis precipitate produced in a filtered solution should give a correct weight after subtraction of filter ash. The common accidental impurity co-precipitated by tannin from tartrate solution is iron, unless the solution has been previously treated with ammonium sulphide (§ 12). In the case of oxalate solutions, the common contaminant is lime, unless the oxalate solution was filtered prior to tannin precipitation. Silica is a frequent impurity, partly derived from the glassware.

The following procedure gives the sum of the three impurities in the ignited pentoxide or other earths: fusion with bisulphate, lixiviation with tartaric acid, treatment of the unfiltered solution with hydrogen sulphide, excess of ammonia, and a few ml. of ammonium chloride and oxalate solutions. After being left to settle on the water-bath, the precipitate is collected, washed with dilute ammonium sulphide solution, and ignited to $(\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO})$. This weight is subtracted from that of the leached precipitate (*vide supra*); needless to say, no allowance for filter ash is made if the impurities are subsequently determined and deducted.

With regard to contamination by silica, attention is drawn to the possible presence of particles of grit, dust or glass in reagents,

even those of A. R. grade. No doubt the particles may find their way into otherwise unexceptionable chemicals subsequent to their preparation. If a reagent is used in the state of solution, the latter is filtered before use. Reagents used in the solid state are re-crystallised from filtered solutions. The bisulphate used as a flux should be specially tested for silica. Hillebrand¹ dissolves 5 g. of bisulphate in a minimum of water, adds 10 ml. of strong sulphuric acid, and evaporates to evolution of white fumes. The cold mass is diluted with 100 ml. of water and the solution filtered. The washed residue is ignited and tested for silica as usual.²

§ 14. Lixiviation of the Bisulphate Melt with Ammonium Oxalate

Solution of a bisulphate melt in oxalate solution is readily achieved. The reagent is a saturated solution of the salt. The quantity of solution used for the leaching should contain a little more of the solid oxalate than the bisulphate flux; we generally take 4 g. of oxalate, or about 80 ml. of saturated solution, to 3 g. of bisulphate. The cold melt, spread against the sides of the crucible, is detached by addition of the hot solvent; after a few minutes' standing the melt can be dislodged with a glass rod and transferred to a 400-ml. beaker; the crucible is rinsed with hot water, ignited and weighed. The balance of the oxalate solution is added to the contents of the beaker, and the liquid is heated to boiling with frequent stirring. No difficulty should be experienced in obtaining a clear solution; occasionally, in cases of extensive expulsion of sulphur trioxide from the pyrosulphate, a few drops of *N* sulphuric acid added to the liquid will assist solution.

We do not use oxalic acid for the solution of bisulphate melts containing earth acids, except in the case of small precipitates composed of earth acids and rare earths (§ 47). Ammonium oxalate is a much better solvent than oxalic acid for tantallic oxide. The ammonium oxalate solution of the bisulphate melt serves for the colorimetric determination of titania in the pentoxides (§ 58).

¹ Hillebrand and Lundell, *op. cit.*, p. 34.

² A frequent cause of contamination by glass particles (see also the interesting article by Tankard and Stock, *Analyst*, 1925, 50, 393, on glass in bottled foods) is the glass stopper of the cheaper kind of reagent bottle, which is not finished off to a smooth rim. Such stoppers easily get chipped when the bottle is opened or closed, especially if any manipulation is required to open the bottle. Unless glass stoppers have well-finished edges, it is preferable to use cork- or rubber-stoppered bottles.

§ 15. Precipitation from Oxalate Solution

The following differences in behaviour between the tartrate and the oxalate solutions of the more important constituents of earth-acid minerals are of analytical interest : (1) precipitation of the earth acids with strong mineral acid (§ 11) is not feasible in oxalate solution ; at least, the precipitation is very incomplete. (2) The tartrate solutions are not precipitated by ammonia ; hence they can be freed from iron by means of ammonium sulphide. This method is not applicable to oxalate solutions, from which most of the earths are precipitated by ammonia (alumina and uranic oxide excepted). (3) Tannin precipitates titanium, zirconium, thorium, iron, aluminium, uranium and the rare earths, together with the earth acids, from the neutralised tartrate solution (§ 84). From almost neutral oxalate solution half-saturated with ammonium chloride, tannin precipitates the earth acids and titanium, but not zirconium, thorium, aluminium and iron (Chapter IX.).

For the quantitative precipitation of the earth acids (and titania), the clear oxalate solution is boiled, cautiously treated with *N* ammonia until the slightest turbidity remains in the still acid solution, diluted with an equal bulk of saturated ammonium chloride solution, and precipitated with tannin as described at greater length in § 49.

§ 16. Centigramme or Milligramme Analysis

The tannin precipitates, on account of their insolubility under proper conditions and their well-defined properties (especially their characteristic colour), are the only earth-acid compounds suitable for quantitative micro- or semimicro-work ; the other earth-acid reactions are not sufficiently sensitive or specific for the purpose.

Our procedure for the detection and determination of traces of earth acids in the filtrates from tannin precipitates may serve as an example of micro-work. While engaged in the researches which resulted in the successful application of tannin to the quantitative analysis of the earths, we have repeatedly searched the filtrates from tannin precipitates for minute amounts of earth acid, so as to satisfy ourselves that the recovery was complete. After standing for a day or more, such filtrates generally deposit a dark flocculent alteration product of tannin, which is almost ash-free, and has not been found to contain earth acid.

The solution is evaporated with 100 ml. of nitric, and 10 ml. of sulphuric acid for the destruction of ammonium salts, tannin and

§ 16 SOLUTION IN HYDROFLUORIC ACID

tartaric (oxalic) acid. When colourless, the acid liquid is transferred to a silica dish in which the evaporation is pushed to complete dryness. The residue, consisting of the bisulphate originally used as a flux, is dissolved in hot water and the solution rendered slightly ammoniacal; the small precipitate is collected, washed and ignited.

The constituents of the precipitate may be silica, earth acid, alumina and ferric oxide; the possible presence of titania should always be taken into account in earth-acid work. The precipitate is heated in the usual manner with hydrofluoric, and a drop of sulphuric acid in a small platinum cup made of foil; the residue is fused with a speck of bisulphate, and the mass dissolved in a ml. or two of ammonium oxalate solution. The liquid—filtered, if turbid, through a tiny pad of filter pulp—is boiled in a 20-ml. beaker and treated with a few mg. of tannin and an equal bulk of saturated ammonium chloride solution; 0.2*N* ammonia is added, drop by drop, from the fine jet of a burette. Near the neutral point the earth acids (and titania) will be precipitated as characteristic yellow to red complexes, whilst iron and alumina remain in solution. If a faint excess of ammonia is added they will be precipitated, iron as a mauve, aluminium as a dirty white complex, soluble on re-acidification. The earth-acid precipitate is collected on a 4- to 5-cm. filter, washed, ignited and weighed; it is once more fused with bisulphate, dissolved by means of a little ammonium oxalate, and the liquid is tested colorimetrically for titania with hydrogen peroxide and sulphuric acid (§ 58).

If it is desired to determine tantalum and niobium separately, the solution which has served for the colorimetric titania determination is evaporated in a beaker with *aqua regia* and a little sulphuric acid for the destruction of ammonium oxalate and hydrogen peroxide. When effervescence has ceased the liquid is transferred to a silica crucible and the heat subsequently raised to fusion of the bisulphate. The cold melt is extracted with a few ml. of a 1 per cent. solution of tannin in 5 per cent. sulphuric acid (§ 54); the earth-acid tannin precipitate is collected, washed, ignited, fused with bisulphate and treated according to § 61 for the separation of tantalum from niobium.

§ 17. Solution in Hydrofluoric Acid : Treatment of the Fluoride Solution

We restrict the application of hydrofluoric acid as a solvent to those earth-acid minerals that contain substantial quantities of rare earths. The other minerals, as well as the pentoxides

themselves or mixtures of pentoxides and other earths, are much more conveniently treated by fusion with bisulphate or alkaline fluxes.

The procedure for solution of earth-acid minerals in hydrofluoric acid is simple. The fine powder (0.25 to 2 g.) is mixed in a platinum or gold vessel with a few drops of water by means of a stout platinum wire, treated with 5 to 10 ml. of strong hydrofluoric acid, and left to stand in the cold or on a water-bath with occasional stirring. The decomposition is usually rapid, and is ascertained by stirring; the dark mineral particles dissolve while a white or greenish precipitate of fluorides separates. The rare-earth fluorides are white; the greenish tinge indicates admixture of uranous fluoride. With minerals that are not readily soluble, the dish or crucible is placed on a water-bath and the liquid kept stirred; fresh acid is added as often as required. When solution is complete, the excess of acid is evaporated and hot water added to form a solution containing about 5 volumes per cent. of hydrofluoric acid. After standing overnight, the precipitate is collected on a filter supported by a rubber funnel and well washed with water containing about 5 per cent. of strong hydrofluoric acid.

This treatment subdivides the constituents of the mineral into two portions, namely (1) an insoluble fraction containing uranous and the rare-earth fluorides, contaminated with subordinate quantities of common elements such as lead, iron and calcium, and (2) a soluble fraction consisting of tantalum, niobium, titanium, zirconium, tungsten, etc. The hydrofluoric acid having done duty in effecting the decomposition of the mineral and, at the same time, a separation of the rare earths from pentoxide and other earths, is then eliminated from both fractions by evaporation with sulphuric acid, which converts the rare earths into sulphates and leaves the earth-acid fraction as a mass soluble in a solution of tartaric acid or ammonium oxalate. Further details on the hydrofluoric-acid method will be found in §§30-33.

CHAPTER V

THE TARTARIC-ACID METHOD FOR THE ANALYSIS OF TANTALONIOBATE MINERALS

THE two introductory paragraphs (18, 19) of this chapter are devoted to a brief discussion of methods of analysis which we have abandoned in favour of the tartaric-acid method. A full description of the latter occupies the remainder of the chapter (§§ 20-29).

§ 18. Inaccuracies of the Pyrosulphate-hydrolysis Method

The most generally applied method for the analysis of tantaloniobate minerals, due to Berzelius, is what we will term pyrosulphate-hydrolysis method, *i.e.*, decomposition of the mineral by fusion with potassium pyrosulphate followed by prolonged boiling of the solution of the melt in order to precipitate the earth acids. The hydrolysis is a tedious and rather uncertain operation: precipitation is not complete if the acidity of the solution is too great, and the completeness of the precipitation is not easily ascertained or ensured. The major drawback of the procedure, however, is the nature of the resultant complex precipitate, which is partly left as an insoluble residue in the extraction of the melt, and partly produced by the more or less gradual flocculation of a colloidal phase; it occludes or adsorbs several of the constituents of the solution, while other elements are partly or wholly co-precipitated. Besides tantalum and niobium, the precipitate may therefore contain tungsten, tin, antimony, lead, iron, silica, titania, zirconia, etc. Being produced in an acid solution, it does not flocculate and settle well as it would from ammoniacal solution; it is partly lumpy, and partly in a very fine state of subdivision, hence filtration and washing are unsatisfactory. Purification of this complex product by solution and re-precipitation by hydrolysis has been attempted, but with indifferent results. Two solvents are discussed in Meyer and Hauser's monograph:¹ acidified hydrogen peroxide, and alkaline mannitol solution.

The second step in the purification of the hydrolysis precipitate was intended to remove tungsten and tin (antimony), and consisted in digestion with ammonium sulphide (Berzelius), or, alternatively, fusion with sodium carbonate and sulphur (Rose). Both processes being faulty in principle, neither had the desired effect.

Any titania present in the mineral, if in substantial quantity, interferes with the quantitative precipitation of the earth acids unless it is itself quantitatively precipitated by suitable reduction of the acidity and sufficiently protracted boiling.

The claim has been advanced for the pyrosulphate-hydrolysis method (Meyer and Hauser, *op. cit.*, p. 271) that it provides a satisfactory separation of zirconia from the earth acids; but it has probably never been

¹ *Die Analyse der seltenen Erden und der Erdsäuren*, p. 274.

substantiated by test separations with the pure oxides. Schoeller and Waterhouse (XII.), in their critical investigation of the method, endeavoured to use it for the separation of zirconia from the earth acids, but came to the conclusion that it was useless for that purpose. Some of their results are reproduced below. The acidity of the liquid is given in g. H_2SO_4 per 100 ml. *HP* denotes the hydrolysis precipitate :

	Taken.		Acidity.	<i>HP</i> .	ZrO_2 in <i>HP</i> .
	g. M_2O_5 .	g. ZrO_2 .			
Ta_2O_5	0.2519	0.2509	1.47	0.3249	0.0815
"	0.2526	0.2542	2.09	0.3222	0.0754
"	0.2522	0.2531	3.43	0.3127	0.0475
"	0.2539	0.2508	4.50	0.2970	0.0325
"	0.2520	0.2512	7.12	0.2632	0.0126
Nb_2O_5	0.2501	0.2521	0.99	0.3304	0.0803
"	0.2500	0.2532	2.0	0.3206	0.0624
"	0.2506	0.2516	2.88	0.3017	0.0509
"	0.2500	0.2528	3.53	0.2830	0.0390
"	0.2516	0.2524	6.46	0.2500	0.0095

Re-treatment of the hydrolysis precipitate, *HP*¹, by the same method gave the following results :

	M_2O_5 .	ZrO_2 .	Acidity.	<i>HP</i> .	ZrO_2 in <i>HP</i> ² .
Ta_2O_5	0.2541	0.2531	3.72	<i>HP</i> ¹ 0.2926	0.0155
			3.60	<i>HP</i> ² 0.2626	
Nb_2O_5	0.2525	0.2518	3.67	<i>HP</i> ¹ 0.2800	0.0112
			3.75	<i>HP</i> ² 0.2531	

Treatment with sulphurous acid of the extraction liquor of the bisulphate melt after Weiss and Landecker¹ resulted in incomplete earth-acid precipitation, yet considerable occlusion of zirconia by the hydrolysis precipitate. Extraction of the bisulphate melt with cold water gave low earth-acid recoveries.

We are satisfied that the pyrosulphate-hydrolysis method cannot be used as a process for the separation of the earth acids from their mineral associates ; it is only a precipitation procedure, and a very poor one at that. With the tartaric-acid method and other processes available, there is no longer any need or justification for its continued use. This evolution in earth-acid analysis has its counterpart in the analytical chemistry of titanium. The time-honoured process for determining that element is the pyrosulphate-hydrolysis method, the diluted sulphate solution being submitted to prolonged boiling under reflux. Accurate methods for the determination of titanium have since been elaborated, so that " in

¹ *Z. anorg. Chem.*, 1909, 64, 72.

§ 18 DRAWBACKS OF ALKALINE FLUXES

view of its many disadvantages, the process may now be considered practically obsolete.”¹

§ 19. Drawbacks of Alkaline Fluxes

We have abandoned the use of alkaline fluxes for the opening up of tantalum- and titanoniobate minerals, because they needlessly complicate the analysis by contamination with metal from the crucible, and are unsuitable for the detection and quantitative recovery of subordinate constituents such as silica, tungsten, tin, lead, and other members of the hydrogen-sulphide group. If the alkaline liquor from the decomposition is to be treated with acid as the next step in the analysis, we argue that the original attack could have been made more simply with an acid flux, without the formation of troublesome silicate, stannate, tungstate, or silicotungstate.

Fusion with Potassium Hydroxide. This flux is advocated by Dr. E. S. Simpson.² The melt is disintegrated with dilute hydrochloric acid, and the earth acids are precipitated by boiling with a definite excess of acid, when they “remain insoluble except in traces.” The precipitate consists of the “hydrates of Ta, Nb (and W?), with all Sb, and at times traces of Mn_2O_4 and SnO_2 . The filtrate contains all Sn, Fe, Mn, Ca, Mg, Cu, Ni, and Ti as chlorides.” The precipitate produced by Simpson’s process is certainly much purer than that obtained in the pyrosulphate-hydrolysis method. Schoeller and Webb (XX.) have made an experimental investigation of Simpson’s process, particularly with regard to the completeness of the earth-acid recovery from the chloride solution and their quantitative separation from tin. We found the earth-acid recovery to result in a loss of 3 to 4 mg. of pentoxide, which is not precipitated by boiling with hydrochloric acid. As regards the separation of tin from the earth acids we found the earth-acid precipitate produced by hydrochloric acid to contain between 1 and 2 mg. of stannic oxide. Hence, while the process achieves a much better separation than the older methods, it gives low results for both earth acids and tin; the former, because they are not quite quantitatively precipitated; the latter, because a small amount of tin remains with the earth acids.

Another factor to be taken into consideration is the contamination of the melt with metal from the crucible. Simpson solves the problem by the rather unattractive expedient of using a nickel crucible for the determination of the metallic acids and metals of the hydrogen-sulphide group, and a silver crucible for that of the earths, uranium, and bases. As to the earth acids and titania, we are not at all sure whether their distribution between the soluble and insoluble fractions after potassium-hydroxide fusion and hydrochloric-acid boiling is as clean-cut as the above quotation would imply.

Fusion with Potassium Carbonate. A valuable paper on the preparation of the earth acids by fusion of the mineral with potassium carbonate in steel crucibles was published by W. B. Giles.³ This process has been erroneously presented by certain compilers as an analytical one.

The reducing conditions under which the fusion is carried out were not intended for the quantitative analysis of earth-acid minerals. In Giles’s own words, “it is not put forward as a quantitative process, but

¹ Thornton, *Titanium*, New York, 1927, p. 91.

² *West Austral. Geol. Survey Bull.*, 23, 1906, p. 72.

³ *Chem. News*, 1909, 99, 1; see § 94.

it certainly yields acids which are much purer than those obtained by fusions with bisulphates. Since the tin and similar metals unite in great part with the vessels used, it is impossible to estimate them even approximately." He does suggest a method for the determination of tin in earth-acid minerals, in which the ore is fused with potassium carbonate in platinum, the melt dissolved in citric acid, and the solution treated with hydrogen sulphide; but this process does not appear to have been thoroughly tested by its author, and it has been adversely criticised by Wells.¹

THE TARTARIC-ACID METHOD

§ 20. Decomposition and Solution of the Mineral

The mineral must be ground to an impalpable powder in an agate mortar. The powder dried at 105° C. is weighed into a tared silica crucible containing dehydrated potassium pyrosulphate. The normal quantity of mineral taken for analysis is 0.5 g.; we do not recommend 1-g. portions for the determination of the major constituents, which can be estimated satisfactorily in 0.25 or even 0.2-g. portions if the supply of material is short. For the proportion of flux to mineral, the manipulations, and re-fusion with sulphuric acid if required, the directions given in § 7 should be followed.

The same remark applies to the lixiviation of the bisulphate melt with tartaric-acid solution. This stage of the process is described in detail in § 8, and the operator is advised to adhere to the directions in order to obtain a clear solution with minerals rich in tantalic acid.

The liquid is filtered through a 7-cm. No. 40 Whatman or No. 0 Munktell filter; it is advisable, if finely divided insoluble matter is present, to press a pad of wet filter pulp into the apex of the filter so that the pad adheres thereto. The insoluble residue is collected on the filter and well washed with small quantities of warm water.

Inspection of the insoluble residue will reveal whether complete decomposition of the mineral has been achieved. If any unattacked particles are visible it is necessary to return the wet filter to the silica crucible, heat it gently on an asbestos mat to dry and subsequently char the paper, and complete the ignition at low temperature. The ignited residue is again subjected to bisulphate fusion and tartaric-acid extraction on a suitably reduced scale, the filtrate being added to that previously obtained.

With minerals containing uranium, the fraction insoluble in tartaric acid will contain lead sulphate. If lead is known or suspected to be present, the solution of the melt should be allowed

Roger C. Wells, *Amer. J. Sci.*, 1911, 31, 436.

§ 20 ANALYSIS OF INSOLUBLE RESIDUE

to stand for some hours in the cold before the insoluble is filtered off. In this case the wash liquor is 0.5 per cent. sulphuric acid, which should be used sparingly. An undue amount of sulphuric acid decreases the recovery of the earth acids by tartaric hydrolysis (§ 25).

§ 21. Analysis of the Insoluble Residue

The residue obtained as in § 20 is normally small, containing probably silica, stannic oxide and lead sulphate. It is first treated with a little hot ammonium or sodium acetate solution for the extraction of the lead sulphate; the acetate filtrate is treated with ammonium sulphide and the lead sulphide is converted into and weighed as sulphate.

The insoluble matter left after the extraction of the lead is gently ignited and weighed as a check. Two alternative procedures are available for its examination: (1) If tin apparently preponderates, the insoluble is reduced by ignition in a porcelain boat in a current of hydrogen; the reduced mass is extracted with hydrochloric acid, the extract is filtered, and the tin is precipitated in the filtrate as sulphide. This is collected, washed with ammonium nitrate solution, calcined and weighed as SnO_2 . The residue from the extraction is ignited, weighed and tested by the normal processes of silicate analysis.

(2) If silica preponderates,¹ the insoluble is fused with sodium

¹ Schoeller and Powell (X.) have tested the accuracy of the separation of silica from the earth acids by the tartaric-acid method by working on mixtures of silica and pentoxides in molecular admixture, obtained by fusing the mixed oxides with 3 g. of potassium carbonate in a platinum dish. The mass was disintegrated with water, acidified with sulphuric acid, and evaporated to dryness; after addition of 2 ml. of strong sulphuric acid, the heat was gradually raised until a bisulphate melt was obtained. After cooling, it was leached with tartaric acid. The solution was filtered, the residue washed with hot water, ignited strongly in a tared platinum crucible, and weighed. After evaporation with hydrofluoric and sulphuric acids, it was again ignited and weighed, the difference giving silica. The bisulphate melt may of course be extracted with oxalic acid or ammonium oxalate. The small residue from the hydrofluoric-acid treatment is once more fused with bisulphate, the melt dissolved in the organic solvent, and the solution added to the main earth-acid filtrate. Results:

Taken.		Residue from Leach.	HF — Residue.	SiO_2 found.	SiO_2 Error.
$\text{g. (Ta, Nb)}_2\text{O}_5$	g. SiO_2				
0.2219	0.0235	0.0254	0.0027	0.0227	— 0.0008
0.2542	0.0575	0.0658	0.0076	0.0582	+ 0.0007
0.3210	0.0208	0.0264	0.0054	0.0210	+ 0.0002
0.5008	0.0139	0.0169	0.0035	0.0134	— 0.0005
0.5022	0.0060	0.0097	0.0036	0.0061	+ 0.0001
None	0.1012	0.1018	—	—	—

carbonate, the mass is disintegrated with water and evaporated with nitric acid (not hydrochloric, as stannic chloride is volatile on evaporation). The insoluble residue from the evaporation to dryness is collected, washed, ignited in a platinum crucible and weighed. The silica is determined as usual by volatilisation, and the residue is tested for tin. Needless to say, hydrogen reduction should not be carried out in a platinum crucible.

The weight of ($\text{SnO}_2 + \text{SiO}_2$) should closely agree with that of the insoluble residue from the extraction of the lead sulphate; if not, the presence of silicate is indicated and the filtrate from the acid evaporation under (2) above should be examined for bases.

§ 22. Determination of Total Stannic Oxide

The next step in the analysis is the determination of the metals of the hydrogen-sulphide group. Before this is described, it should be mentioned that a number of native tantaloniobates, especially tantalite and columbite, do not as a rule contain members of that group other than tin. Stannic oxide is attacked to a slight extent by molten pyrosulphate, hence a few mg. of tin find their way into the tartrate solution. In absence of lead and metals of the hydrogen-sulphide group, the determination of silica and total stannic oxide is carried out in one operation,¹ as follows:

The unfiltered tartrate solution from the lixiviation of the bisulphate melt is treated in a 250-ml. beaker with 5 ml. of 10 per cent. sulphuric acid, a few ml. of 1 per cent. mercuric chloride solution (optional), and a current of hydrogen sulphide at about

¹ The separation of tin from the earth acids by the method here described has been worked out and tested by Schoeller and Webb (XX.), who obtained the results reproduced below. In the first five experiments the weight of the first tin fraction P^1 was determined because it shows the amount of earth acid left in the residue from the first operation. In the last two experiments the tin was obtained in two separate fractions, namely as SnO_2 insoluble after double bisulphate fusion and tartaric-acid leaching (under R^2), and the ignited sulphide precipitate obtained in the combined filtrates from R^1 and R^2 (under SP).

	Taken		P^1	P^2	SnO_2 Error.
	g. M_2O_3	g SnO_2			
Ta	0.1232	0.0543	0.0564	0.0543	0.0000
"	0.2534	0.0204	0.0440	0.0204	0.0000
"	0.1558	0.0642	0.0708	0.0633	- 0.0009 (a)
Nb	0.2013	0.0202	0.0230	0.0211	+ 0.0009
"	0.1555	0.0499	0.0542	0.0498	- 0.0001
			R^2	SP	
Ta + Nb	0.2083	0.0435	0.0350	0.0083	- 0.0002
"	0.2130	0.0227	0.0131	0.0099	+ 0.0003

(a) A small amount of SnO_2 was detected in the Ta_2O_5 recovered from the filtrate, by a repetition of the above procedure.

50° C. The liquid saturated with the gas is left to itself in a warm place until the precipitate has settled; it is filtered through a 7-cm. paper containing a pad of filter pulp in its apex. The precipitate P^1 is collected, washed with hydrogen-sulphide water containing a few drops of sulphuric acid, gently ignited in a tared silica crucible, and weighed. It contains the whole of the tin, with silica, and possibly a small residual admixture of earth acid. This is removed by re-treatment with smaller amounts of bisulphate and tartaric acid, precipitation with hydrogen sulphide, etc., as before. The precipitate, P^2 , is again ignited and weighed. Loss in weight indicates elimination of earth acid, in which case the filtrate from P^2 is worked up separately as in § 24. The weighed precipitate P^2 is analysed as under (1) or (2), § 21.

§ 23. Precipitation of Metals of the Hydrogen-sulphide Group

The clear filtrate or combined filtrate from the insoluble residue obtained in § 20 is saturated at 50° C. with hydrogen sulphide, and left in a warm place for an hour to clear. The sulphide precipitate, SP^1 , is collected and washed with hydrogen-sulphide water containing a few drops of sulphuric acid; the filtrate is reserved, or concentrated by evaporation (see § 25).

The precipitate, if substantial, usually contains a few mg. of earth (more especially tantallic) acid, co-precipitated probably by the flocculation of a little colloidal earth-acid derived from the tartaric complexes by dissociation. The flocculation is no doubt assisted, or perhaps induced, by that of the sulphide precipitate. The precipitate SP^1 should be worked up by the following procedure,¹ which effects the recovery of any earth acid it may

¹ Method of Waterhouse and Schoeller (XXII.). The results given below are reproduced from their paper.

	Taken.		Recovered, g. Sb ₂ O ₃ .	Error.
	g. M ₂ O ₃ .	g. Sb ₂ O ₃ .		
Ta	0.2638	0.0238	0.0238	0.0000
"	0.2022	0.0618	0.0616	- 0.0002
Nb	0.2169	0.0607	0.0614	+ 0.0007
"	0.1720	0.1152	0.1144	- 0.0008
		g. Bi ₂ O ₃ .	g. Bi ₂ O ₃ .	
Ta	0.1780	0.1024	0.1025	+ 0.0001
"	0.1370	0.1284	0.1271	- 0.0013
Nb	0.2089	0.1826	0.1834	+ 0.0008
"	0.1006	0.1497	0.1486	- 0.0011
		g. CuO.	g. CuO.	
Ta	0.1400	0.0502	0.0500	- 0.0002
Nb	0.2039	0.0675	0.0670	- 0.0005

contain, and at the same time a separation of the antimony sub-group from the copper sub-group.

Treatment of SP^1 . Filter and precipitate are returned to the beaker and warmed with 8 ml. of strong sulphuric acid, with repeated cautious addition of nitric acid, until the organic matter is destroyed. The oxidant is completely expelled by strong heating. The mass, when cold, is treated with 10 ml. of 20 per cent. tartaric-acid solution and 25 ml. of warm water. Ammonia in moderate excess is added, and the liquid is slowly poured into fresh ammonium polysulphide solution. The covered beaker is allowed to stand on a covered water-bath for an hour or more.

Treatment of SP^2 (Copper Sub-group). If sulphides insoluble in ammonium sulphide (SP^2) have separated, they are collected, washed with dilute ammonium sulphide solution, and dissolved in dilute nitric acid, which is evaporated. The dry residue is taken up with a little hot 10 per cent. nitric acid; the liquid is filtered through a small paper containing a pad of filter pulp. Washing is effected with 10 per cent. acid. The filtrate is analysed for bismuth and copper (traces of lead) by the usual methods; the filter and pad (which may contain traces of earth acid) are ignited in a tared platinum crucible, *C*, reserved for other earth-acid fractions (see §§ 24, 25).

Precipitation of SP^3 (Antimony Sub-group). The clear yellow ammonium sulphide solution, or filtrate from SP^2 , is acidified with acetic acid, boiled, treated with hydrogen sulphide, and left to clear. The precipitate, SP^3 , is collected and washed as before, and the filtrate is treated as in § 24. SP^3 is returned to the beaker with the paper and heated with 8 to 10 ml. of strong sulphuric acid and 2 g. of potassium bisulphate until the mass is perfectly colourless. After dilution, cooling and suitable acidification with hydrochloric acid, the antimony is titrated with permanganate. The titrated liquid is treated with *ferrum reductum*, and the antimony precipitate is examined for copper (cupric sulphide is slightly soluble in ammonium polysulphide). The filtrate from the antimony precipitate is treated with hydrogen sulphide for the determination of a minor tin fraction (*i.e.*, dissolved in the bisulphate fusion).

§ 24. Recovery of Earth Acids from Tartrate Solution by Tannin Precipitation

The tartrate filtrate from SP^3 (§ 23) contains the few mg. of earth acid (if any) occluded in SP^1 . The filtrate could be added to that from SP^1 . We recommend, however, to work it up separately, as its inclusion with the main filtrate would

§ 24 PRECIPITATION OF METALLIC ACIDS

substantially increase the quantity of sulphuric and tartaric acids in the combined filtrate. This is undesirable in tartaric hydrolysis (§ 25); on the other hand, the recovery of the small quantity of earth acid occluded in SP^1 is readily effected as follows:

The filtrate from SP^3 (or from P^2 , § 22) is boiled for the removal of hydrogen sulphide. The free acid is then neutralised to litmus with ammonia; the solution is treated with 5 g. each of ammonium chloride and acetate, boiled, and precipitated with a fresh solution of 0.5 g. of tannin. The coloured precipitate flocculates after short boiling, and is collected on a No. 41 Whatman filter (9 or 11 cm.). It is washed with 5 per cent. ammonium chloride solution, and ignited in the tared platinum crucible C reserved for earth acids (§§ 23, 25). The filtrate from the tannin precipitate is discarded.

The niobium precipitate is orange- to brownish-red, whilst the tantalum complex (which should be pale yellow) has usually a mauve hue, due to contamination with traces of iron.

Schoeller and Webb (XVII.), who worked out this method, found the following results:

	Taken : g. M_2O_5 .	TP (gross).	TP (net).	Error.
Ta	0.0104	0.0107	0.0100	- 0.0004
"	0.0052	0.0061	0.0054	+ 0.0002
Nb	0.0073	0.0084	0.0071	- 0.0002
Ta + Nb	0.0068	0.0087	0.0072	+ 0.0004
"	0.0178	0.0205	0.0175	- 0.0003
"	0.0102	0.0130	0.0099	- 0.0003

The ignited precipitates were purified as under § 13 (*d*), (*e*). The "gross" weight is the weight of the precipitate before purification, the "net" weight that of the purified precipitate.

A convenient way of preparing a neutral tartrate solution previous to tannin precipitation of the earth acids and other earths (§ 84) consists in boiling the slightly ammoniacal solution until the free ammonia is expelled. The solution is treated with ammonium chloride and acetate, a slight excess of ammonia, and boiled until it no longer smells of ammonia. It is then treated with 2 or 3 drops of dilute acetic acid and precipitated while boiling with tannin.

§ 25. Precipitation of Tantallic, Niobic and Tungstic Acids (Major Fraction) by Tartaric Hydrolysis

The filtrate from SP^1 (§ 23) is evaporated to 150 ml., and once more treated with hydrogen sulphide, if yellow, for the conversion

of ferric into ferrous salt. The solution is boiled, stirred and treated with 25 ml. of strong hydrochloric acid, an operation already described in § 11. After three minutes' boiling, the precipitate, *HP*, is allowed to settle, collected on an 11-cm. No. 40 Whatman paper containing some filter pulp, returned to the beaker with 2 per cent. ammonium chloride solution and washed as directed in § 13 (*a*). (Filtrate : see § 26.) The precipitate is ignited in the tared platinum crucible *C* (§§ 23, 24), and weighed as a guide. It is undesirable to purify the precipitate at this stage ; the determination of tungstic oxide in *HP* is described in § 38.

Tartaric hydrolysis, first described by Schoeller and Deering (IX.), is a valuable earth-acid reaction. In qualitative analysis, it is a specific and sensitive test for their joint detection (§ 89) ; in the quantitative analysis of earth-acid minerals by the tartaric-acid method, it forms a convenient means for removing the major portion of the three metallic acids from the solution at a suitable stage.

Schoeller and Webb (XVI.) have investigated the reaction quantitatively. They found that four mineral associates of the earth acids (Ti, Zr, Th, U) interfere to a certain extent. The following results should be studied for the sake of a better understanding of the reaction.

(1) The precipitation of the *earth acids* is never quite quantitative :

	Taken.	<i>HP</i> .	Recovery Error.
g. Ta_2O_5	0.2003	0.1985	— 0.0018
„	0.1065	0.1052	— 0.0013
„	0.0110	0.0100	— 0.0010
Nb_2O_5	0.1014	0.0927	— 0.0087
„	0.0111	0.0104	— 0.0007

(2) With *nitric acid* as the precipitant, *tungstic oxide* reacts like the earth acids :

	Taken.	<i>HP</i> .	Error.
g. WO_3	0.1000	0.0952	— 0.0048
„	0.1000	0.0934	— 0.0066

The tungsten precipitate is yellow and settles well. When *hydrochloric acid* is used, the tungsten precipitation is less complete than with nitric acid ; preponderating quantities of earth acid, however, induce precipitation of tungstic acid to such an extent that Schoeller and Waterhouse (XXXI.) use tartaric hydrolysis under standardised conditions for the determination of tungsten in earth-acid minerals (see § 40).

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TARTARIC HYDROLYSIS

The tungsten recovery decreases with increasing concentration of *sulphate* and *tartaric acid* (XXVI.):

Taken.		HP.	WO ₃ in HP.	Used.	
g. (Ta, Nb) ₂ O ₅ .	g. WO ₃ .			KHSO ₄ .	C ₄ H ₆ O ₆ .
0.1510	0.0148	0.1623	0.0127	3 g.	3 g.
0.1507	0.0150	0.1584	0.0107	4 g.	6 g.

(3) *Oxalic acid* should not be present, otherwise the precipitation is very incomplete:

Taken.		HP.	
g. (Ta, Nb) ₂ O ₅			
0.2025	0.2060	0.1117	{ in presence of 1 g. amm. oxalate.
„	„	0.1289	

(4) *Sulphuric acid* acts like oxalic acid in decreasing the earth-acid recovery (IX.):

g. M ₂ O ₃ taken.		Added.	HP.	Error.
Ta	0.1010	30 ml. HNO ₃ + 15 ml. H ₂ SO ₄	0.0931	- 0.0079
„	0.1013	30 „ HCl + 15 „ „	0.0647	- 0.0366
Nb	0.1023	30 „ HNO ₃ + 15 „ „	0.0606	- 0.0417
„	0.1009	30 „ HCl + 15 „ „	0.0672	- 0.0337

With the usual quantities of bisulphate and tartaric acid (3 to 4 g. of either reagent), with oxalic acid absent and sulphuric acid (washings of sulphide precipitates) kept at a minimum, tartaric hydrolysis by hydrochloric or nitric acid normally results in a shortage of a few mg. of pentoxides, as does Simpson's procedure outlined in § 19 (precipitation of the earth acids from alkaline solution by boiling with hydrochloric acid) (XX.).

(5) *Titanium*. With small quantities of pentoxides and titania (a few cg.), very little titania is occluded in *HP*, with the result that an approximate separation of titania from the earth acids is achieved (Chapter X, § 53). Re-treatment of the first *HP* furnishes another precipitate, *HP*², still lower in titania, at the cost of an increased earth-acid loss:

G. taken.		HP ¹ .	HP ² .	TiO ₂ in HP ¹ .	
(Ta, Nb) ₂ O ₅ .	TiO ₂ .				
0.0620	0.0307	0.0606	0.0587	0.0013	{ Analyses by Lundell and Knowles (IX.).
0.0602	0.0325	0.0599	0.0577	0.0011	

The amount of co-precipitated titania increases with the quantities of reacting oxides (IX.) :

	G. taken.		HP ¹ .	HP ² .	TiO ₂ in HP ¹ .
	M ₂ O ₅ .	TiO ₂ .			
Ta	0.1007	0.1020	0.1136	0.1028	0.0040
Nb	0.1090	0.1555	0.1224	0.1038	0.0036
„	0.2016	0.2005	0.2592	0.2136	0.0260
„	0.3996	0.0341	0.4063	0.3886	0.0022

(6) *Zirconia*. The recovery of tantalic oxide in *HP* is strongly affected by large amounts of zirconia, the tantalum recovery being low, and *HP* contaminated with zirconia. The recovery of niobic oxide does not decrease to the same extent with an increase in zirconia, though *HP* is contaminated as in the case of tantalic oxide. The mixed pentoxides react in presence of zirconia like niobic oxide. Schoeller and Webb (XVII.) have published twenty-nine experiments on the interference of zirconia in tartaric hydrolysis, of which four are given here :

	G. taken.		HP.	ZrO ₂ in HP.
	M ₂ O ₅ .	ZrO ₂ .		
Ta	0.1017	0.0216	0.1040	0.0090
„	0.1030	0.0520	0.0775	0.0112
Nb	0.1028	0.0429	0.0984	0.0104
Ta + Nb	0.1018	0.0732	0.1018	0.0206

(7) *Thoria*. The interference of thoria in tartaric hydrolysis is slight compared with that of zirconia (XXVIII.) :

	G. taken.		ThO ₂ in HP.
	M ₂ O ₅ .	ThO ₂ .	
Ta	0.2028	0.0239	0.0034
Nb	0.2048	0.0223	0.0022

(8) *Uranic Oxide*. Schoeller and Webb (XXV.) found that the precipitation of tantalic oxide in presence of substantial amounts of uranium proceeded normally, but that *HP* occluded a small amount of uranium ; whereas the precipitation of niobic oxide under the same conditions was less quantitative and resulted in a precipitate free

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AMMONIUM-SULPHIDE GROUP

from uranium. The mixed oxides behave in this case like tantalum oxide :

	G. taken.		HP.	U_3O_8 in HP.
	M_2O_5 .	U_3O_8 .		
Ta	0.2042	0.1515	0.2038	0.0042
Nb	0.1999	0.1599	0.1436	nil
Ta + Nb	0.1017	0.2018	0.0950	0.002

(9) *Complex oxide mixtures* containing the three metallic acids and substantial amounts of the above four oxides (as far as they have been tested) conform to the rule that tartaric hydrolysis furnishes a precipitate containing the major fraction of the metallic acids and a certain amount of co-precipitated oxides. This contamination is immaterial, as *HP* (after extraction of the tungstic oxide) is added to the balance of the earths obtained as explained in Chapter IX, § 48.

What tartaric hydrolysis achieves is the removal of the metallic acids from a purified solution (silica, tin, lead, and soluble metals of the H_2S -group having been eliminated) in the form of a precipitate free from iron, manganese, rare earths, alumina, beryllia, lime, and magnesia. These elements have been proved not to be co-precipitated.

(10) *Phosphoric Acid*. Whilst phosphoric acid is not a constituent of earth-acid minerals proper, it may be stated here that the earth-acid precipitate produced by tartaric hydrolysis occludes small quantities of phosphoric acid fairly completely (Schoeller and Webb (XXXII.)) :

	G. taken.		HP.	P_2O_5 in HP.
	M_2O_5 .	P_2O_5 .		
Ta	0.2514	0.0062	0.2560	0.0054
Nb	0.2505	0.0063	0.2412	0.0055

The determination of phosphoric acid in certain minerals is discussed in § 34.

§ 26. Precipitation of Iron and Manganese as Sulphides

The filtrate from *HP*, § 25, is boiled down to small bulk in an 800-ml. beaker and transferred to a 250-ml. beaker, in which it is evaporated to about 20 ml. The ferric salt in the solution is reduced with hydrogen sulphide, whereupon the liquid is treated with a decided excess of fairly strong ammonia and 10 ml. of fresh ammonium sulphide. The precipitate, which contains the iron and usually all but 1 to 3 mg. (sometimes the whole) of the manganese, is allowed to settle for some hours in a warm place, then collected on a 9-cm. No. 40 Whatman filter containing some filter pulp, and well washed with warm water containing ammonium sulphide and chloride. (Filtrate : § 27.)

The washed sulphide precipitate is ignited in a small porcelain dish and dissolved by warming with a few ml. of hydrochloric acid. After addition of 0.25 to 0.5 g. of ammonium chloride, the solution is evaporated to dryness. In our experiments the crystalline residue always dissolved in cold water to a clear solution: hence it was free from earth acid. The chloride solution is transferred to a 400-ml. beaker, treated with ammonium acetate, diluted to about 150 ml., and heated to incipient boiling; the basic acetate precipitate is collected, washed, dissolved in hydrochloric acid, the iron is re-precipitated with ammonia, and the precipitate is ignited to Fe_2O_3 . The filtrate from the basic acetate precipitate is treated with ammonium chloride and phosphate; the precipitate is ignited to $\text{Mn}_2\text{P}_2\text{O}_7$.

The precipitation of ferrous sulphide from ammoniacal tartrate solution is the first application of tartaric acid in mineral analysis, having been devised by Berzelius for the separation of iron from aluminium. The iron is quantitatively precipitated; it should be reduced to the ferrous condition before precipitation, as ferrous sulphide does not occlude the earths present.

The precipitation of manganous sulphide from ammoniacal tartrate solution has been the subject of conflicting statements in the literature, it being generally understood that manganese is incompletely precipitated under such conditions. An investigation by Schoeller and Webb (XXVII.) confirmed the singular behaviour of manganese towards ammonium sulphide in tartrate solution. Solutions prepared from pure manganous salt were readily and quantitatively precipitated; application of the procedure to a manganotantalite gave erratic results. The finely powdered mineral was fused with bisulphate, and the melt was dissolved in tartaric-acid solution. The liquid was saturated with hydrogen sulphide, and filtered. The bulk of the earth acids was then eliminated by tartaric hydrolysis with 30 ml. of hydrochloric acid; the filtrate from *HP*, containing all the manganese and iron, was precipitated with ammonia and ammonium sulphide. Under varying test conditions, the manganese recoveries varied from almost *nil* to over 95 per cent., but the cause or causes of the variations remained obscure, Schoeller and Webb expressing the opinion that the present state of knowledge of the nature of metal solutions in tartaric or other organic acids is too imperfect to afford theoretical guidance in the problem under discussion. They observed that dilution tended to prevent precipitation, and were thus led to work in concentrated solutions. As a result, more or less complete recoveries were achieved at high concentrations. The manganotantalite assayed 12.30 per cent. of manganous oxide, and the following recoveries were effected by evaporation of the filtrate from *HP* to about 20 ml. previous to treatment with ammonia and ammonium sulphide:

Took 0.5 g. of mineral (four tests).

	1.	2.	3.	4.
Found:	0.0891	0.0891	0.0894	0.0902 g. $\text{SnO}_2 + \text{SiO}_2$.
	0.3166	0.3199	0.3160	0.3130 g. <i>HP</i> .
	0.0224	0.0222	0.0226	0.0227 g. Fe_2O_3 .
	11.69	11.36	11.79	12.30 per cent. MnO .

The evaporation to small bulk of the filtrate from *HP* fulfils a double purpose : it eliminates the greater part of the hydrochloric acid added as a precipitant for the earth acids, and induces more complete precipitation of the manganese. It is probable that, when iron preponderates over manganese, the former will induce quantitative precipitation of the latter in a small volume of solution. The small amount of manganese that escapes precipitation as sulphide finds its way into the filtrate containing lime and magnesia, where it can be recovered by the usual methods. The sulphide precipitate may have to be tested for nickel and zinc, which have been reported in small quantities in a few minerals. Like manganese, they are separated from iron by the basic acetate method.

§ 27. Concluding Stages of the Tartaric-acid Method : Choice of Procedures

We will at this point survey the operations described in this chapter by tabulating the elements found in tantaloniobate minerals (alkalis, fluorine and water excepted)¹ as follows :

PRECIPITATED.	STILL IN SOLUTION.
<i>Group 1.</i>	<i>Group 4.</i>
Silica, tin, lead.	Lime.
Hydrogen-sulphide group.	Magnesia.
Iron (zinc, nickel).	Manganese (minor).
Manganese (major).....	
<i>Group 2 (HP).</i>	<i>Group 3 (AP).</i>
Earth acids (major).....	Earth acids (minor).
Tungstic acid.....	Tungstic acid (traces).
Small quantities of these oxides may be occluded }..... { in <i>HP</i> (§ 25).	Titania, zirconia. Uranic oxide. Thoria. Rare earths. Alumina, beryllia.

Group 1 comprises the insoluble fraction and the metals removed as sulphides ; *group 2*, the constituents and impurities of the hydrolysis precipitate. *Groups 3* and *4* are still contained in the tartrate filtrate, *group 3* being separable as an ammonia precipitate, *AP*, from *group 4* after destruction of the tartaric acid. *Groups 2* and *3* comprise all the earths with tungstic and uranic oxides ; the quantitative resolution of this complex mixture forms the subject of Part II (Chapters VII–XII).

In the concluding stages of the tartaric-acid method, it will be convenient to distinguish two cases, according to the nature of the mineral under treatment. This may be either a simple

¹ These constituents must be determined in separate portions by the usual methods.

mineral, such as tantalite, columbite, strüverite, ilmenorutile, stibiotantalite or bismutotantalite; or a more complex mineral, such as microlite, samarskite, yttrotantalite, fergusonite, etc., liable to contain the majority of the constituents of group 3. The former case is discussed in § 28, the latter in § 29.

§ 28. Procedure for Simple Minerals (Schoeller and Webb (XXVII.).)

The filtrate from the sulphide precipitate (§ 26) contains the minor fraction of the earth acids and the major fraction of the titania. They are recovered from the tartrate solution by tannin precipitation, the solution being boiled until the ammonium sulphide is destroyed and acidified with 2 or 3 drops of acetic acid, etc., as described in § 24. The tannin precipitate, *TP*, is ignited, and added to the earth acids freed from tungstic acid by the magnesia method (§ 38); the combined precipitate is then freed from titania (if present in quantities exceeding a few mg.) by the oxalate-salicylate method (§ 55); finally, the earth acids are separated from each other by the tannin method (§ 61).

The filtrate from *TP* is practically free from mineral constituents. It should, however, be tested for common metals or bases (including lime and magnesia) by the following sequence of operations: (1) destruction of ammonium chloride, tannin and tartaric acid, by nitric and sulphuric acids (§ 10); (2) evaporation of the acid mass in a silica dish until the original bisulphate melt is obtained; and (3) solution of the melt in water and successive treatment with ammonium hydroxide, sulphide, oxalate and phosphate.

§ 29. Procedure for Complex Minerals

It is assumed that some or all of the members of Group 3, § 27, are present.

The filtrate from the sulphide precipitate (§ 26) is boiled down and treated as in § 28 for the destruction of ammonium chloride and organic compounds. The acid liquor is transferred to a silica dish or crucible and evaporated until the original bisulphate melt remains. The cold mass is dissolved in warm water and the warm liquid, which may be cloudy, is treated with an excess of ammonia (§ 87, *c*). The precipitate, *AP*, is collected, washed with 1 per cent. ammonia solution containing very little ammonium chloride, dissolved, and reprecipitated as before. The precipitate is then treated with hydrofluoric acid as described in § 44, or ignited, etc., as in § 45 (Chapter VIII).

The combined filtrate from *AP* is tested for lime, magnesia and manganese (minor fraction).

CHAPTER VI

THE HYDROFLUORIC-ACID METHOD FOR THE ANALYSIS OF TITANONIOBATE MINERALS OF THE RARE EARTHS. OTHER METHODS OF ANALYSIS

THE analytical methods described in the present chapter have not been subjected by us to any extensive investigation in the laboratory. The text of J. Lawrence Smith's hydrofluoric-acid method (§§ 30-32), however, has benefited by the criticism of Dr. Roger C. Wells, Chief Chemist of the U.S. Geological Survey Laboratory, Washington.

§ 30. The Hydrofluoric-acid Method

The original paper by J. L. Smith¹ gives only a very brief description of this valuable process. Its chief advantages are, that the rare-earth minerals are more or less readily decomposed, and that a quantitative separation of the rare earths from the earth acids is effected in the process of decomposition. In the words of Hillebrand and Lundell,² "When applicable it should always be used, for it affords very quickly and easily an almost perfect separation of the insoluble rare-earth and alkaline-earth fluorides from the soluble fluorides of the earth-acid and other metals. The method introduces no alkali salts and has the further advantage, shared by no other, not only of showing whether quadrivalent uranium is present but also of separating it quantitatively from sexivalent uranium if both are present."

Smith's method was used and modified by Hillebrand.³ The improvements introduced by him relate more particularly to the separation of the earth acids from the other constituents of the soluble fluoride fraction by a process of hydrolytic precipitation which is now advantageously replaced by our tartaric-acid method.⁴ Hillebrand observed that the "treatment with HF at once reveals whether the Fe is present as admixed hematite or limonite . . . or is chemically combined with the acids of the mineral. In the first case it resists the solvent action of HF for some time after the tantalates and columbates are thoroughly decomposed." The presence of these iron minerals indicates alteration in the titanoniobate mineral.

An important contribution to the study of Smith's method has been made by Dr. R. C. Wells,⁵ with whose courteous permission I reproduce the summation of an analysis of samarskite showing the quantitative distribution of the constituents between the soluble and insoluble

¹ *Amer. Chem. J.*, 1883, 5, 73.

² *Op. cit.*, p. 466.

³ *Colo. Sci. Soc. Proc.*, 1888, 3, 38.

⁴ Hillebrand and Lundell, *op. cit.*, p. 468.

⁵ *J. Amer. Chem. Soc.*, 1928, 50, 1017.

fluoride fractions. Dr. Wells remarks that the method "is not as simple or clean-cut in its separations as the original description might lead one to suppose"; but his figures show that the separation of the metallic acids from the rare earths is quantitative. The constituents found in both fractions are all common elements. In the directions given below I have largely drawn on the observations recorded in Dr. Wells's paper and in Hillebrand and Lundell's treatise, though in the treatment of the soluble fluoride fraction (§ 33) I have proceeded along the lines of the tartaric-acid method (Chapter V).

Analysis of Samarskite by Dr. R. C. Wells.

	Insoluble in HF.	Soluble in HF.	Total.
Nb ₂ O ₅ . . .	—	41.00	41.00
Ta ₂ O ₅ . . .	—	4.62	4.62
TiO ₂ . . .	—	2.20	2.20
SnO ₂ . . .	—	0.04	0.04
WO ₃ . . .	—	0.02	0.02
UO ₂ . . .	5.83	—	6.14*
UO ₃ . . .	—	2.41	2.08*
Ce ₂ O ₃ . . .	0.20	—	0.20
(La, Tb) ₂ O ₃ . . .	4.56	—	4.56
Y ₂ O ₃ , etc. . .	27.54	—	27.54
ThO ₂ . . .	1.55	—	1.55
ZrO ₂ . . .	—	0.02	0.02
Fe ₂ O ₃ . . .	0.71	2.33	3.04
MnO . . .	0.20	0.47	0.67
ZnO . . .	0.06	0.03	0.09
Ba, Sr . . .	—	—	traces
CaO . . .	2.57	0.05	2.62
MgO . . .	0.13	0.04	0.17
PbO . . .	0.84	0.02	0.86
K ₂ O . . .	0.10	0.11	0.21
Na ₂ O . . .	0.04	0.06	0.10
H ₂ O . . .	—	1.31	1.31
Undetermined . . .	0.30	0.25	0.55
He . . .	—	—	present
Total per cent.			99.69

* Stage of oxidation based on titration with KMnO₄.

§ 31. Solution of the Mineral

The mineral is ground to an impalpable powder. Smith used 5-g. portions, no doubt with the intention of obtaining sufficient earth acid for the separation of tantalum from niobium by Marignac's method. Both Hillebrand and Wells reduced the weight of mineral to 2 g. With the more sensitive processes now at our disposal, the determination of all but the very subordinate

constituents can be made on 0.5 g., or even less if the supply of material is limited. Silica, if present, must be determined in a separate portion by the tartaric-acid method (§ 21), as it volatilises in the treatment with hydrofluoric acid.

The powder (0.5 g.) is moistened with water and covered with strong hydrofluoric acid in a platinum dish, and digested first in the cold, then on the steam bath. If the mineral is rather refractory, repeated evaporation with fresh portions of acid and frequent stirring with a platinum rod are necessary. The operator will be guided by the disappearance of the particles of original mineral. When decomposition is complete, the acid is evaporated down to less than 5 ml., and diluted with water to about 100 ml. The liquid is stirred and left overnight. The solution is decanted through a 9-cm. filter supported by a rubber funnel; the precipitate is washed, by decantation first, with water acidulated with hydrofluoric acid. If not more than one platinum dish is available, the filtrate is collected in a vulcanite or bakelite vessel, and reserved (see § 33). The fluoride precipitate is rinsed back into the platinum dish; the filter paper is gently ignited, and the ash is added to the precipitate (see next §).

§ 32. Treatment of the Insoluble (Rare-earth) Fraction

This consists of the fluorides of the rare earths, thorium, quadrivalent uranium, nearly all of the calcium and lead, and small quantities of occluded common elements (see Analysis, § 30). The suspension of the precipitate is evaporated with 12 ml. of 1 : 1 sulphuric, and a little nitric acid (to oxidise the uranium) until the liquid fumes freely. After cooling, the acid is diluted with 20 ml. of water, and the evaporation to strong fumes is repeated to ensure complete removal of the hydrofluoric acid.

The residual acid mass is transferred from the platinum dish to a beaker containing 50 ml. of cold water. The dish is rinsed with 50 ml. of warm water, and discarded. The liquid on standing may deposit lead sulphate. This is collected on a small filter, washed, and treated with hot ammonium acetate solution, which should produce a clear solution, indicating complete removal of the earth acids from the fluoride precipitate by washing. The lead is recovered from the acetate solution by means of ammonium sulphide.

The filtrate from the lead sulphate is saturated with hydrogen sulphide; if a small precipitate of lead sulphide forms, it is left to settle, collected, washed, and added to the bulk. The lead sulphide may be converted to chromate, and determined ^{gravimetrically} idiomatically, or to sulphate, and weighed.

The filtrate from the lead sulphide is boiled, and oxidised with nitric acid. It is treated in the usual way with ammonium chloride and hydroxide (see § 87, *c*) ; the precipitate is collected, washed, dissolved in hydrochloric acid, and re-precipitated. A third precipitation may be advisable to avoid contamination of the rare earths with alkaline earths. The ammoniacal filtrates are combined, slightly acidified, concentrated by evaporation, and once more made feebly ammoniacal. If a slight precipitate forms, it is collected and added to the main ammonia precipitate ; the filtrate (*x*) is added to the corresponding filtrate obtained from the soluble fraction (see § 33).

The ammonia precipitate contains the rare earths, thoria, the uranium originally in the lower state of oxidation, and a little iron. It is dissolved in nitric acid, and the solution evaporated short of complete dryness. The residue is dissolved in water, and the rare earths and thoria are precipitated as oxalates, the solution being poured into oxalic acid solution. The precipitate is submitted to the usual processes of rare-earth analysis : the thoria is separated from the rare earths by thiosulphate precipitation.¹ The rare earths are separated by means of sodium sulphate into the cerium-terbium group (insoluble double sulphates) and the yttrium group (soluble double sulphates).² Ceria is determined in the cerium group by a volumetric process.³

The filtrate from the oxalate precipitate is treated with excess of ammonium carbonate and a few ml. of fresh ammonium sulphide, and left to stand until the ferrous sulphide has settled. This is collected, washed as usual, ignited, and reserved (see *y*, § 33). The filtrate from the sulphide precipitate is evaporated to dryness, and the residue is gently ignited and dissolved in nitric acid. The solution is filtered (platinum derived from the dish may remain insoluble at this stage). The filtrate is precipitated with ammonia ; the precipitate is ignited and weighed as U_3O_8 , which is reported as UO_2 . It should be tested for silica, and perhaps beryllia (§ 67).

Dr. Wells quotes Hillebrand to the effect that it seems doubtful whether the distribution of the uranium between the insoluble and soluble fluoride fractions obtained by Smith's method corresponds exactly with the uranous and uranic oxide contents of the mineral. Hence Wells considers it advisable " to express the reducing power of the mineral, as determined by solution in

¹ Hillebrand and Lundell, *op. cit.*, p. 422. Dr. Wells prefers the peroxy-nitrate method as being simpler.

² *Ibid.*, p. 439.

³ Metzger, *J. Amer. Chem. Soc.*, 1909, 31, 523.

sulphuric acid or sodium bisulphate ¹ in a sealed tube and titration with permanganate, first as UO_2 and any remaining as FeO ."

Hillebrand and Lundell ² adopt the following course of treatment for the ammonia precipitate. It is dissolved in a small excess of hydrochloric acid and the solution is precipitated with oxalic acid, sufficient ammonium oxalate being added to neutralise the greater part of the free hydrochloric acid. The oxalate precipitate, OP^1 , is collected and washed with 1 per cent. oxalic acid. If uranium is present, the precipitation with oxalic acid is repeated, OP^1 being treated with fuming nitric acid, or ignited and dissolved in hydrochloric acid. Re-precipitation with oxalic acid yields OP^2 , which is reserved.

The filtrate or combined filtrate from the oxalates is evaporated to dryness, and the oxalic acid destroyed by heating; the further treatment of the residue depends on the absence or presence of uranium.

If *uranium is absent*, the residue is once more dissolved in a slight excess of hydrochloric acid, and the small balance of rare earths is precipitated in concentrated solution with oxalic acid; the precipitate, OP^3 , is added to OP^2 ; the filtrate is precipitated with ammonia and the precipitate, if any (Fe , Zr), added to γ , § 33.

If *uranium is present*, Hillebrand and Lundell give preference to a hydrofluoric acid separation process. The residue from the destruction of the oxalic acid by ignition in a platinum dish is taken up in hydrofluoric acid, which is then evaporated nearly to dryness. What remains insoluble is collected, washed with water containing a little hydrofluoric acid, and heated together with the filter with sulphuric and nitric acids until the organic matter is destroyed. The sulphate solution is precipitated with oxalic acid, and the small precipitate, OP^3 , added to OP^2 . The fluoride filtrate, containing the uranium, is heated with sulphuric acid until all the hydrofluoric acid is expelled. The sulphate mass is taken up in dilute nitric acid, the uranium is precipitated with ammonia, and the precipitate is ignited to U_3O_8 . It should be tested for the possible presence of iron and zirconium. The net weight of the U_3O_8 is calculated to UO_2 .

§ 33. Treatment of the Soluble (Earth-acid) Fraction

The soluble fraction contains tantalum, niobium, tungsten, tin, titanium, zirconium, sexivalent uranium, beryllium, and the bulk

¹ In a private communication, Dr. Wells states that he has had no trouble in treating minerals with bisulphate in sealed evacuated pyrex glass tubes in a nearly horizontal position. Attack with sulphuric acid alone is slow.

² *Op. cit.*, p. 467.

of the iron and other common metals including the alkalis. We will distinguish two cases : (a) the alkalis and the earths are to be determined in one and the same portion ; and (b) the alkalis are determined in a separate portion. If sufficient material is available, a separate alkali determination by decomposition of the mineral with calcium carbonate and ammonium chloride (method of J. L. Smith) is more convenient and accurate.

(a) *Determination of Alkalis and Earths in the Same Portion.*

The filtrate from the fluoride precipitate (§ 31) is evaporated in a platinum dish with 10 ml. of sulphuric acid until strong white fumes are given off. After cooling, dilution with water, and renewed heating until a large part of the sulphuric acid has been driven off, the acid mass is stirred and diluted with water, and digested hot for an hour. The precipitate is mixed with filter pulp, collected, and washed with water containing a little ammonium nitrate. The filtrate is precipitated hot with a small excess of ammonia ; the precipitate thus obtained is collected like the preceding, the two precipitates are ignited together or in succession in a silica crucible, and fused with 4 g. of potassium bisulphate ; the further treatment of the melt is discussed under (c) below.

The filtrate from the ammonia precipitate is added to the filtrate *x* obtained in § 32, and the liquid is examined for manganese, zinc, alkaline earths, and alkalis by known methods.

(b) *Determination of the Alkalis in a Separate Portion.* In this case the filtrate from the fluoride precipitate (§ 31) is evaporated twice with sulphuric acid in a platinum dish as under (a), but 3 g. of potassium bisulphate are added in the second evaporation, and the liquid is heated until the free sulphuric acid is expelled and a bisulphate melt remains. This is treated as under (c) below.

(c) The bisulphate melt from (a) or (b) is dissolved in tartaric acid solution with the precautions observed in § 20 ; the solution is saturated with hydrogen sulphide, and the precipitate is analysed for tin and traces of lead. This is best carried out as follows : the sulphide precipitate is collected on a small pad of filter pulp, and washed with water containing a little hydrogen sulphide and sulphuric acid. The precipitate is transferred with the pad to a small conical flask, the funnel is rinsed with water, and the liquid is boiled down with a few ml. of sulphuric acid. Heating is continued until the acid is colourless. Any platinum sulphide present is thus reduced to spongy metal. The acid mass is diluted, and digested at moderate heat with a little hydrochloric acid ; the platinum is filtered off and washed with hot ammonium acetate solution. The tin and lead in the filtrate

are once more precipitated as sulphides, and separated by treatment with sodium sulphide.

The subsequent stages of the analysis of the soluble fraction are the same as those of the tartaric-acid method, viz., tartaric hydrolysis (§ 25), precipitation of the ammonium sulphide group (§ 26)—the small ferruginous precipitate γ from § 32 having been fused with a little bisulphate and the solution added to the filtrate from *HP*—and destruction of the tartaric acid and ammonium chloride followed by precipitation with ammonia (§ 29). Needless to say, the ammonia precipitate, being free from thorium and rare earths, is not subjected to the operations described in Chapter VIII.

OTHER METHODS OF ANALYSIS

§ 34. Analysis of Minerals Akin to Zircon

These comprise silicates such as naegite, hagatalite (see Chapter III). Minerals of this class may contain subordinate amounts of rare earths, thorium, uranium, and earth acid. It would appear desirable, in view of the observations of Kimura,¹ to provide for the determination of phosphoric acid in the analytical scheme.

For the analysis of silicate minerals related to zircon we favour high-temperature decomposition by alkali carbonate, because they are not readily attacked by fused bisulphate; the objections cited in § 19 against the use of an alkaline flux do not apply in the case of zirconium silicate poor in earth acid and free from tin and tungsten. Besides, a scheme including the determination of phosphoric acid should avoid an initial fusion with bisulphate as this may result in a certain amount of volatilisation loss of phosphoric acid.²

The scheme outlined below utilises Powell and Schoeller's process³ for decomposing zircon or Brazilian zirconia rock, i.e., fusion with sodium carbonate followed by bisulphate fusion of the residue from the carbonate fusion, instead of simple bisulphate fusion as hitherto practised.

It may not be out of place here to give a brief outline of Powell and Schoeller's scheme. The melt from the carbonate fusion is extracted with water; the acidified filtrate is evaporated to dryness for silica, and the residue digested with dilute acid. The residue from the carbonate fusion is fused with potassium bisulphate, and the product is dissolved in water and a little sulphuric acid. The two extracts are filtered, and the combined filtrates (*a*) reserved. The combined residues are ignited and weighed before and after treatment with hydrofluoric and sulphuric acids, silica being determined by difference. The small fixed residue from the last treatment is once more fused with bisulphate, and the solution of the melt is added to the combined filtrates (*a*).

¹ Kimura, *Japan. J. Chem.*, 1925, 2, 73.

² Hillebrand and Lundell, *J. Amer. Chem. Soc.*, 1920, 42, 2609.

³ *Analyst*, 1919, 44, 397.

The solution thus obtained is treated with hydrogen sulphide, neutralised with sodium carbonate, and boiled with sodium thiosulphate; the precipitate, *HP*, is $(\text{ZrO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3)$. It is fused with sodium carbonate, and the alumina is determined in the aqueous extract; titania is determined colorimetrically in the residue from the carbonate fusion, and zirconia is taken by difference. The filtrate from *HP* is analysed for any iron, manganese, lime, and magnesia.

Whilst this simple process answers well for ordinary zircon, and can even be made to include the determination of thorium and phosphoric acid (the former appearing in *HP* and the latter in the filtrate from the sodium carbonate fusion), it is hardly suitable for minerals containing also earth acids, rare earths, and uranium. The scheme given below departs from the above process once the decomposition of the mineral has been effected by successive fusions with alkali carbonate and bisulphate.

Decomposition of the Mineral. The finely powdered mineral (0.5 g.) is ignited in a tared platinum crucible, and the loss on ignition is determined. The material is then fused with 5 g. of sodium carbonate for an hour or more in the covered crucible. The melt is extracted with hot water and a little sodium hydroxide (two to three pellets), and the extract (*a*) is filtered into a porcelain dish; the crucible is rinsed, and the residue washed, with 2 per cent. sodium carbonate solution. The residue is returned to the dish in which the extraction was made, and digested hot with a little *N* hydrochloric acid; the solution is made ammoniacal, filtered through the same paper, and the precipitate is collected and washed with 0.5 per cent. ammonium chloride solution. The filtrate (*b*) is acidified, concentrated, and reserved.

It may be advisable to repeat the above operations, residue and filter being ignited in the platinum crucible and fused with 3 g. of sodium carbonate. The extract (*a*) is added to the first; the residue is again treated with *N* acid and ammonia, and collected (*c*); the filtrate (*b*) is added to the first.

Treatment of Filtrate (a). The liquid is acidified with hydrochloric acid and evaporated for the recovery of silica (first fraction) by the usual method (*d*). It is best to repeat the evaporation to dryness of the filtrate for the recovery of a little additional silica.

The filtrate from the silica contains the phosphoric acid, with some uranium and perhaps aluminium. It is precipitated by magnesia mixture in presence of citric acid,¹ the precipitation being repeated. The combined filtrates are neutralised with hydrochloric acid, boiled, and precipitated with tannin and ammonium acetate (§ 68). The tannin precipitate is ignited and reserved (*e*).

¹ Hillebrand and Lundell, *op. cit.*, 566.

Treatment of Residue (c). After ignition in a silica crucible, this residue is fused with 3 to 4 g. of bisulphate. The melt is digested with 100 ml. of warm 0.1 *N* sulphuric acid, and the residue is collected and washed with slightly acidulated water. It represents the second silica fraction, which is combined with the first (*d*), strongly ignited in the tared platinum crucible, and weighed. It is treated as usual with sulphuric and hydrofluoric acids, and the dry residue is again ignited and weighed, silica being found by difference. The small fixed residue (*f*) is fused with a little bisulphate.

The filtered extract from the main bisulphate fusion, to which is added the solution of melt (*f*) (a slight turbidity is immaterial), is treated with ammonia chloride (5 g.), and precipitated hot with a slight excess of ammonia (double treatment). This yields a precipitate (*g*) and a filtrate which, after addition of the filtrate (*b*), is analysed for lime and magnesia, and possibly a little manganese.

Treatment of Precipitate (g). The constituents of the precipitates are: thoria and rare earths; iron; zirconia, earth acids, titania; and the balance of uranium and aluminium. The precipitate is ignited in a silica crucible, fused with bisulphate, and the melt is leached with 100 ml. of warm 5 per cent. oxalic acid solution (§ 45). The crucible is rinsed with a little water, the solution is left overnight, and the residue is collected and analysed for thoria and rare earths.

The filtrate, after addition of 2 to 3 g. of tartaric acid, is treated with hydrogen sulphide, made ammoniacal, and left to itself overnight. The ferrous sulphide is collected and converted as usual into Fe_2O_3 .

The ammoniacal tartrate filtrate is treated with sulphuric acid (1 : 1) so as to contain 10 per cent. of free acid, freed from hydrogen sulphide by boiling, carefully cooled, and precipitated with a slight excess of cupferron in fresh, filtered 6 per cent. solution.¹ The precipitate, consisting of zirconia with subordinate quantities of earth acid and titania, is mixed with filter pulp, collected under slight suction, washed with *N* hydrochloric acid, and ignited and weighed in a silica crucible. The separation of the four earths is described in Chapters IX to XI.

The cupferron filtrate is boiled with 10 c.c. of nitric acid for the destruction of the cupferron, made ammoniacal, boiled, and precipitated with tannin. The precipitate is collected, ignited, combined with fraction (*e*), and analysed for uranium and aluminium.

¹ Hillebrand and Lundell, *op. cit.*, 110.

Notes. (1) While the detection of phosphoric acid in minerals containing earth acid is under discussion, it may be opportune to describe a process worked out by Schoeller and Webb (XXXII.) for the separation of small quantities of phosphoric acid in earth-acid precipitates (P_2O_5 is occluded in the tartaric-hydrolysis precipitate: see § 25).

The oxide is fused with sodium hydroxide in a nickel crucible, and the product is extracted with half-saturated sodium chloride solution, as in the separation of the earth acids from tungstic oxide (§ 39). The liquid is filtered through a tight pad of filter pulp, and the precipitate is washed with half-saturated sodium chloride solution. The filtrate is precipitated with magnesia mixture in presence of citric acid as above, the precipitate being dissolved and re-precipitated. The following results were obtained with mixtures of earth acid and potassium dihydrogen phosphate.

	G. taken.		G. found.		P_2O_5 Error.
	$Mg_2O_8.$	$P_2O_5.$	$Mg_2P_2O_7.$	$P_2O_5.$	
Ta	0.2509	0.0064	0.0097	0.0062	— 0.0002
Nb	0.2532	0.0081	0.0124	0.0079	— 0.0002
Ta	0.3027	0.0127	0.0194	0.0124	— 0.0003
Nb	0.3118	0.0057	0.0090	0.0057	0.0000

(2) The extraction of the bisulphate melt of the ammonia precipitate with oxalic acid is an adaptation of the method proposed by Pied¹ for the separation of the rare earths from the earth acids. The process was studied and criticised by Schoeller and Waterhouse (XXVIII.), whose conclusions will be found under § 45. They limit the application of the process to small quantities (a few cg.) of the reacting oxides. Hence it should prove serviceable for the analysis of zirconia precipitates containing subordinate amounts of earth acid, thoria, and rare earths.

(3) Cupferron as a precipitant for the earth acids was first proposed by Pied (*loc. cit.*), and studied by Lundell and Knowles in co-operation with Schoeller and Webb (XVII.). Exps. 1 to 4 by Lundell and Knowles, on a decigramme scale, showed that the precipitation involved a very slight negative error; Exps. 5 to 8 (Schoeller and Webb), on a cg. scale, gave somewhat similar results:

Exp.		G. Mg_2O_8 taken.	Found.	Error.
1	Nb	0.1936	0.1930	— 0.0006
2	„	0.1947	0.1942	— 0.0005
3	Ta	0.1962	0.1961	— 0.0001
4	„	0.1955	0.1946	— 0.0009
5	„	0.0210	0.0210	0.0000
6	„	0.0283	0.0278	— 0.0005
7	Nb	0.0251	0.0249	— 0.0002
8	„	0.0285	0.0285	0.0000

¹ *Comptes rend.*, 1924, 179, 897.

By applying the micro-test described in § 16, Schoeller and Jahn (XXVI.) detected minute amounts of earth acid in the cupferron filtrates.

For the precipitation of the earth acids we give preference to tannin over cupferron, as tannin is cheaper, stabler, more easily procurable, and non-poisonous, besides being a perfect precipitant of the earth acids. On the other hand, cupferron is a valuable reagent for the analysis of tannin group B (Chapter II., 9) as it precipitates zirconium (hafnium), but does not precipitate aluminium or sexivalent uranium (quadrivalent uranium is precipitated). In the analysis described above, cupferron collects the minor constituents, earth acid and titania, in the zirconium precipitate.

§ 35. Analysis of Eudialyte and Related Minerals

These silicates, rich in lime and soda, are soluble in hydrochloric acid. The following simple method for their analysis is given by R. Mauzelius in Doelter's Handbook.¹

The powdered mineral is attacked with hydrochloric acid, and the acid is evaporated to complete dryness, etc., for the determination of silica. This is ignited, weighed, and volatilised in known manner. The weighed residue is fused with bisulphate, the insoluble portion from the extraction of the melt with water consisting of earth acid; the filtrate from the earth acids yields a small ammonia precipitate, which is dissolved in hydrochloric acid and added to the filtrate from the silica. This is precipitated with ammonia and a little hydrogen peroxide, yielding a precipitate—of dioxide earths and rare earths, with iron and manganese—and a filtrate containing lime, magnesia, and soda.

The ammonia precipitate is dissolved in hydrochloric acid, the acid is evaporated, and the aqueous solution is precipitated with oxalic acid. The precipitate is analysed for thorium and rare earths. The oxalate filtrate is treated with tartaric acid, hydrogen sulphide, and ammonia, iron and manganese being precipitated.² The filtrate is evaporated and the residue ignited for the destruction of the organic acids, fused with bisulphate, and the melt is dissolved in dilute sulphuric acid. This solution is precipitated with ammonia, the precipitate consisting of zirconia and titania; the ammoniacal filtrate may contain a little more lime, occluded in the original ammonia precipitate.

Chlorine is determined in the mineral by solution in dilute nitric acid, dilution, filtration, and precipitation of the filtrate with silver nitrate.

¹ *Handbuch der Mineralchemie*, Vol. III., Part I., 152.

² Cf. § 26 on the precipitation of manganese.

§ 36. Analysis of Tantaliferous Tin Minerals (Ainalite, etc.)

The simplest and cleanest method for the decomposition of tin ore—*i.e.*, ignition in hydrogen—is also the best for the analysis of varieties of cassiterite containing tantalic (niobic) oxide. The alternative to reduction would be fusion with an alkaline flux, a mode of working beset with difficulties.

The reduction is carried out in a porcelain boat placed in a combustion tube: the boat remains unattacked, hence there is no contamination. We prefer a boat to a Rose crucible, as the progress of the reduction can be watched and the operation is under better control (XX.). The temperature is regulated to a moderate red heat, and the ignition is interrupted when the powder has been converted into small, grey metallic globules. The boat is left to cool under hydrogen, and its contents are transferred to a beaker; the reduced material is extracted with hydrochloric acid (1 : 3 water), and the extract is filtered. The insoluble fraction is ignited, returned to the boat, and ignition in hydrogen and extraction with acid are repeated. The combined extract is partially neutralised with ammonia and precipitated with hydrogen sulphide; the precipitate contains the tin, and the filtrate is tested for iron.

The insoluble residue from the second extraction is ignited in a tared silica crucible, weighed, and fused with bisulphate; the melt is extracted with tartaric acid, and the analysis of the soluble and insoluble portions is conducted substantially as described in Chapter V.

PART II

QUANTITATIVE SEPARATION METHODS

Introduction

THE quantitative separation methods described in Part II (Chapters VII to XII) form a consecutive series of operations, intended to resolve into its constituents a complex mixture of oxides obtained in the analysis of earth-acid minerals by the tartaric-acid method, or by other means from a variety of ores or alloys.

The separation methods here described are confined to elements occurring in earth-acid minerals, and obtained therefrom by two successive group precipitations tabulated in § 27, namely :

(1) *The tartaric-hydrolysis precipitate, HP (Group 2), containing the crude tungstic and earth acids ; and*

(2) *The ammonia precipitate, AP (Group 3), containing the minor fraction of the earth acids ; titania, zirconia (hafnia), thoria ; rare earths ; alumina, beryllia ; and uranic oxide.*

Iron and all metals precipitable as sulphides from tartrate solution are not considered here ; nor are the alkaline earths, which are obtained in the filtrate from AP.

For the quantitative separation of the above elements I have proposed the following scheme (XXXIII.) :

(1) *Determination of tungstic oxide in HP, and recovery of the earth acids and co-precipitated earths (see Chapter VII).*

(2) *Separation of thoria and rare earths from the other constituents of AP (see Chapter VIII).*

(3) *Addition of AP, freed from thoria and rare earths, to the recovered earth acids from HP, and separation of the mixture into two tannin groups : Group A (titania and earth acids) ; Group B (zirconia, alumina, beryllia, uranic oxide) (see Chapter IX).*

(4) *Separation of titania from the earth acids (see Chapter X).*

(5) *Separation of tantalum from niobium (see Chapter XI).*

(6) *Separation of zirconium, aluminium, beryllium, and uranium (see Chapter XII).*

CHAPTER VII

THE SEPARATION OF TUNGSTIC OXIDE FROM THE EARTHS

Introduction

THE methods described in this chapter apply to the separation of tungsten from the earths precipitated by tartaric hydrolysis, tantalic and niobic oxides being the major, titania and zirconia the minor, constituents of *HP* (§ 25); minute quantities of thoria and uranic oxide also may occur in the precipitate if plentiful in the mineral. The magnesia method (§ 38) provides a separation of tungsten from these elements; it must be supplemented by sodium hydroxide fusion if niobium is present in quantity (§ 39).

In the case of earth-acid minerals free from titanium and zirconium, tungstic oxide may be separated from the earth acids by the sodium-chloride method (§ 41): the procedure allows an approximate preliminary determination of tantalum and niobium to be made (§ 5).

For tungstic oxide in association with the necessary excess of earth acids, tartaric hydrolysis provides a separation from aluminium, beryllium, rare earths, iron, and manganese; the determination of tungsten in earth-acid minerals by tartaric hydrolysis is described in § 40.

Iron may be separated from tungsten by precipitation as sulphide from tartrate solution (§ 26). The other elements of the ammonium sulphide group may be collected in the ferrous sulphide precipitate.

§ 37. Determination of Tungstic Oxide by the Tannin Cinchonine Method

The precipitation of tungstic oxide from alkaline tungstate solution by tannin and a mineral acid, first described by Schoeller and Jahn (VII.), represents a great advance in tungsten analysis, as it provides an accurate and convenient method for the determination of small quantities of tungsten in solutions containing much alkali chloride or other salts. In this respect it is superior to the mercurous-nitrate method, which is impracticable in presence of substantial amounts of chloride, besides requiring a very delicate adjustment. For some time past, precipitation by alkaloids (*e.g.*, cinchonine) has found increased favour. The drawback of these reagents is that the presence of alkali salts is undesirable. Cremer ¹ found that in such a case forty-eight hours was required for the

¹ *Eng. Min. Journal*, 1895, 59, 345.

cinchonine precipitate to settle. The useful rule that delayed precipitation means more or less incomplete recovery was borne out in this case, the cinchonine recovery showing negative errors of 1 to several mg. in presence of much alkali salt.

While investigating the application of tannin to the determination of tungsten, we found that its recovery in form of the bulky brown tannin complex was not quite quantitative, but that the brown coloration of the filtrate rendered visible the few mg. that had escaped precipitation. It was argued that this small fraction must be in colloidal suspension, therefore amenable to co-precipitation by tannin precipitants such as alkaloids. This inference proved correct, as addition of a little cinchonine hydrochloride solution to the brown suspension of the tungsten-tannin complex produced a flocculent precipitate containing the whole of the tungsten :

Exp.	G. WO_3 taken.	WO_3 found.	Error.
1	0.0532	0.0536	+ 0.0004
2	0.0044	0.0047	+ 0.0003
3	0.0229	0.0233	+ 0.0004
4	0.0444	0.0443	- 0.0001

In this procedure the presence of alkali salt, far from being prejudicial, is desirable, as it promotes flocculation.

Two years after the publication of Schoeller and Jahn's paper, Moser and Blaustein¹ described a process for the determination of tungsten based on exactly the same principle, namely, complete flocculation of the tungsten-tannin complex by an alkaloidal reagent; with this unessential difference, that they employ antipyrin instead of cinchonine. In introducing their method, they state (without giving the reference to our paper) that we had previously observed the incomplete precipitation of tungsten by tannin, but that we succeeded in precipitating the balance with cinchonine; and that the latter reagent, proposed by Cremer (*loc. cit.*) for the precipitation of tungsten, rendered the use of tannin really unnecessary.

If the reader will refer to the original text of Section VII., he will be able to satisfy himself that Moser and Blaustein's comments are an obvious misinterpretation of our work.

Procedure. The alkaline or ammoniacal tungstate solution (100 to 200 ml.), containing alkali or ammonium chloride, is treated at 50° C. with a fresh solution of 0.5 g. of tannin, part of which flocculates as a white precipitate if the chloride ion concentration is high. The solution is treated with dilute hydrochloric acid until acid to litmus paper, when the tannin dissolves while the brown turbidity due to the tungsten complex appears. A thin cream of filter pulp is added, followed by 5 ml. of a 5 per cent. solution of cinchonine in dilute hydrochloric acid and added

¹ *Monatsh. Chem.*, 1929, 52, 351.

drop by drop while the liquid is briskly stirred, the tungsten complex blending thoroughly with the cinchonine tannate and the filter fibre. After standing cold for some hours or overnight, the liquid is decanted through a loose filter (No. 41 Whatman, 11 cm.); filtration is exceedingly quick, and the filtrate is perfectly clear. The matted precipitate is squeezed in the beaker with a glass rod or, if on the filter, it is returned to the beaker with a jet of wash-liquor (cold 5 per cent. ammonium chloride solution containing a little cinchonine), and stirred up with 100 ml. of the same. The edge of the filter is well washed for the removal of alkali salt; the precipitate is again collected, and the washing completed.

After draining, the wet precipitate is heated in a tared porcelain crucible on an asbestos mat until the paper is charred; the ignition is then completed at low temperature on a triangle. The yellow residue is allowed to cool, and weighed as WO_3 .

§ 38. Separation of Tungstic Oxide from the Earths by the Magnesia Method

This process, worked out and tested by Powell, Schoeller, and Jahn (XXIX.), is an adaptation of Bedford's method for the analysis of a niobotungstate.¹ Bedford fused the mixed oxides with potassium carbonate and treated the solution of the melt with excess of magnesia mixture; the precipitate was collected, washed with a solution of the precipitant, ignited, and fused with bisulphate; the mass was boiled with water, and the precipitate collected, ignited, and weighed as Nb_2O_5 , tungstic oxide being obtained by difference.

We succeeded in utilising Bedford's reaction for the separation of tungsten from titanium, niobium, tantalum, and zirconium, recovering the earths as a mixed tannin precipitate, and determining the tungsten by our tannin-cinchonine method. We proved, moreover, that Bedford's process gives a less perfect separation of tungstic oxide from niobic oxide than from the other earths, a few mg. of niobium passing into the tungsten filtrate. Large quantities of titanium or tantalum counteract this tendency. We recommend a purity test on the recovered tungstic oxide, *i.e.*, application of the method described in § 39.

Procedure. The mixed oxides (0.2 to 0.5 g.) are fused with 4 g. of potassium carbonate in a platinum crucible over a strong burner for ten to fifteen minutes. The fused mass is taken up in 150 to 200 ml. of hot water, care being taken to disintegrate any lumps by gentle boiling and manipulation with a glass rod. The crucible is rinsed and discarded, and the hot solution is treated with freshly-prepared reagent (1 g. of crystallised magnesium sulphate, 2 g. of ammonium chloride, 25 ml. of water, 4 drops of ammonia). The covered beaker is kept on a covered water-bath for half an hour. The flocculent precipitate is collected on an

¹ *J. Amer. Chem. Soc.*, 1905, 27, 1216.

11-cm. filter, and washed with quarter-saturated ammonium chloride solution.

The precipitate is rinsed back with the same wash-solution; the filter is ignited, and the ash is added to the liquid. The suspension (150 ml.) is acidified with hydrochloric acid and digested on the water-bath for an hour. An equal volume of saturated ammonium chloride solution is then added, and the reaction is adjusted to slight acidity to litmus paper with dilute ammonia. The liquid is now treated with 2 g. of ammonium acetate and heated to boiling, and fresh 5 per cent. tannin solution is added until flocculation is complete. The precipitate, TP^1 , is allowed to settle on the water-bath, collected with the help of gentle suction, washed with the ammonium chloride solution, and ignited in a platinum crucible.

If TP^1 requires re-treatment, it is again fused with potassium carbonate, and the operations above described are repeated, yielding a second magnesia precipitate and a filtrate therefrom, which is added to the first. The magnesia precipitate is again treated with tannin as for TP^1 , giving TP^2 , which is ignited and weighed as mixed earths.

The filtrate or combined filtrate from the magnesia precipitate or precipitates is treated with 50 ml. of saturated ammonium chloride solution, and treated by the tannin-cinchonine method (§ 37) for tungsten.

If the mineral contains uranium, part of this element follows the tungsten into the alkaline filtrate obtained in the magnesia method. Both metals give a brown tannin precipitate, the uranium complex readily dissolving when the liquid is acidified prior to the addition of cinchonine. When the tungsten precipitate has been filtered off, the uranium is recovered from the filtrate by precipitation with ammonia.

The following results were obtained by Powell, Schoeller and Jahn (XXIX.) in the separation of binary mixtures by the magnesia method :

Exp.	G. taken.		WO ₃ found in		WO ₃ Error.
	WO ₃ .	Earth.	First treatment.	Re-treatment.	
1	0.0310	None	0.0311	—	+ 0.0001
2	0.0337	TiO ₂ 0.2078	0.0281	0.0047	— 0.0009
3	0.0236	Nb ₂ O ₅ 0.2536	0.0266	0.0235	— 0.0001
4	0.0259	Ta ₂ O ₅ 0.2274	0.0247	0.0011	— 0.0001
5	0.0316	ZrO ₂ 0.2898	0.0320	—	+ 0.0004

It will be seen that the separation of tungstic oxide from the three earths other than zirconia required double treatment. In the case of tantalum and titanium, the recovered earth was re-treated as described above ; in the case of niobium, the tungstic oxide obtained by a single treatment had to be purified (§ 39).

Tests made on ternary and more complex mixtures gave results reproduced below :

Exp.	G. taken.		G. found.	Errors.
	WO ₃ .	Earths.		
6	0·0324	TiO ₂ 0·1547	WO ₃ 0·0320	- 0·0004
		Nb ₂ O ₅ 0·1546		
		Sum 0·3093	Earths 0·3095	+ 0·0002
7	0·0341	TiO ₂ 0·2130	WO ₃ 0·0337	- 0·0004
		Nb ₂ O ₅ 0·2074		
		Sum 0·4204	Earths 0·4202	- 0·0002
8	0·0242	TiO ₂ 0·2027	WO ₃ 0·0225	- 0·0017
		Ta ₂ O ₅ 0·2032		
		Sum 0·4059	Earths 0·4072	+ 0·0013
9	0·0228	TiO ₂ 0·2027	WO ₃ 0·0228	0·0000
		Ta ₂ O ₅ 0·2020		
		Sum 0·4047	Earths 0·4045	- 0·0002
10	0·0315	TiO ₂ 0·0788	WO ₃ 0·0312	- 0·0003
		Nb ₂ O ₅ 0·1134		
		Ta ₂ O ₅ 0·0902		
		ZrO ₂ 0·1020		
		Sum 0·3844		

In Exps. 6 to 10, the tests with titania and niobic oxide were very successful in a single treatment. In the next two experiments (titania and tantalic oxide), No. 8 gave a negative tungsten, and a positive tantalum, error in a single treatment ; in Exp. 9, the separation succeeded in one treatment, in which the precipitant was added at about 50° C., and the further heating of the suspension of the magnesia precipitate was omitted. The more complex mixture (Exp. 10) was successfully treated in a single operation ; we ascribe this to the presence of niobic oxide, zirconia being quite inert in the magnesia method.

§ 39. Separation of Tungstic Oxide from Niobic (and Tantalic) Oxide by Fusion with Sodium Hydroxide

This method was originally devised by Schoeller and Jahn (VIII.) for the determination of small amounts of earth acids in tungstic oxide (see (a) below) ; it was subsequently found to be a useful adjunct to the magnesia method, as it frees the tungstic oxide from the small amounts of niobium with which it may be contaminated after application of the magnesia method to niobium-rich oxide mixtures (see (b)).

Procedure. (a) Small Quantities of Earth Acid in Tungstic Oxide. The oxide (1 g.) is fused with sodium hydroxide (2 g.) in a nickel crucible. In order to avoid dusting caused by the strong action of the melting alkali upon the tungstic oxide, we moisten the oxides and alkali in the crucible with a few drops of water, and dry the contents by gentle heating ; the bulk of the oxide is thus dissolved before the water is expelled. The fluid melt is brought to a red heat, which need not be maintained for more than half a minute. The cold mass is taken up in the crucible with 10 ml. of half-saturated sodium chloride solution by digestion on a hot plate for a few minutes, and the liquid is allowed to stand a few hours in the cold. A little filter pulp is stirred in, and the small precipitate is collected on a small, tightly packed pad of filter pulp in a small funnel ; it is washed with the sodium chloride solution (1 to 1.5 ml. at a time) till the washings hardly blue litmus paper (eight to ten times). The pulp containing the precipitate is rinsed into a 50-ml. beaker, and digested hot with a few drops of dilute hydrochloric acid for half an hour ; it is collected on a small filter, washed with dilute ammonium chloride solution, and ignited to $(Ta, Nb)_2O_5$. Tungstic oxide, as the predominant constituent, is taken by difference.

(b) Purification of Tungstic Oxide separated from Niobic Oxide and other Earths by the Magnesia Method. The procedure is the same as the preceding, but on a smaller scale. The weighed tungstic oxide obtained in § 38 is transferred to a nickel crucible and fused with two to six pellets of sodium hydroxide to a dull red for less than a minute. The attack on the crucible is negligible. The clear melt is left to cool, and extracted with half-saturated sodium chloride solution ; the liquid is filtered, etc., as under (a). The tungsten in the filtrate is precipitated by the tannin cinchonine method (§ 37) ; the small earth-acid precipitate is treated as under (a) above, and added to the earths recovered by tannin from the magnesia precipitate (§ 38).

By applying Method (a), Schoeller and Jahn obtained the following results in their test analyses :

	G. taken.		M_2O_5 found.	Error.
	M_2O_5	WO_3		
Nb_2O_5	0.0108	1.000	0.0107	— 0.0001
„	0.0083	1.000	0.0082	— 0.0001
Ta_2O_5	0.0062	1.000	0.0061	— 0.0001
$(Ta,Nb)_2O_5$	0.0018	1.000	0.0019	+ 0.0001

§ 40. Determination of Tungsten in Earth-acid Minerals

The essential directions for the determination of tungsten in earth-acid minerals have already been given (see *Procedure*, below). What remains to be discussed in this paragraph is the calculation of the tungstic-oxide content of the mineral on the basis of the analytical result, as the process does not give a full quantitative recovery; nor have we been able to elaborate a more efficient method.

The investigations of Schoeller and Jahn (XXVI.) have proved that tungsten is an interfering element in tannin or cupferron precipitations of the earth acids from tartrate or oxalate solutions. This is due to the stability of tartaro- and oxalotungstic acids, which by themselves are not decomposed by tannin or cupferron. The stability is not sufficiently high for separation purposes, for preponderating quantities of earth acid induce incomplete precipitation of the tungsten, which thus distributes itself over the precipitates and filtrates. In Exps. 1 to 4 below, tannin was used as the precipitant (TP = tannin precipitate); cupferron was applied in Exps. 5 to 8 (KP = cupferron precipitate). In the tannin precipitation tests, niobium induced more pronounced tungsten precipitation than did tantalum, the reverse being the case in the cupferron tests:

Exp.	G. taken			TP	WO_3 in TP .
	M_2O_5		WO_3		
1	Ta_2O_5	0.2006	0.0148	0.2098	0.0094 } tartrate
2	Nb_2O_5	0.2041	0.0150	0.2193	0.0124 } solution
3	Ta_2O_5	0.2016	0.0152	0.2087	0.0078 } oxalate
4	Nb_2O_5	0.2021	0.0150	0.2162	0.0132 } solution
				KP	WO_3 in KP .
5	Ta_2O_5	0.2000	0.0153	0.2111	0.0137 } tartrate
6	Nb_2O_5	0.2037	0.0158	0.2080	0.0049 } solution
7	Ta_2O_5	0.2018	0.0150	0.2122	0.0126 } oxalate
8	Nb_2O_5	0.2009	0.0158	0.2045	0.0041 } solution

The above tests made it evident that tungsten must be eliminated from the mixed earths prior to their separation from each other by any processes involving the use of tannin or cupferron. This problem was investigated by Schoeller and Waterhouse (XXXI.), who finally concluded that the precipitation of tungstic acid with the earth acids by tartaric hydrolysis is probably the only means of recovering the bulk of the tungsten from tartrate solution (major tungsten fraction). The recovery being incomplete (see tests, § 25, 2), we proceeded to locate the minor tungsten fraction not precipitated by tartaric hydrolysis. Several processes were evolved, two of which were thoroughly tested, namely, induced ammonia precipitation, and double tartaric hydrolysis.¹

The latter process gave an almost complete recovery in some cases, though at the cost of much extra manipulation. We decided, therefore, that for practical purposes the determination of tungsten in earth-acid minerals should be confined to the recovery of the major fraction by tartaric hydrolysis. If we could improve the tungsten recovery in the major fraction it would hardly be worth while doing a disproportionate amount of work, and perhaps vitiating the determination of the remaining constituents, for the sake of an incomplete recovery of the minor tungsten fraction. The amount of the latter might be estimated more closely by computation on the basis of experimental data.

Additional tests aiming at a higher recovery in the major fraction proved fairly successful, thanks to standardised conditions of precipitation at higher concentration. We were able to prove, moreover, that *tantalic oxide induces almost quantitative precipitation* of tungstic acid (Exp. 1 below), whereas *niobic oxide* (which is itself less completely precipitated) *collects tungstic oxide less efficiently* than does tantalalic oxide (Exp. 5). If tantalum preponderates over niobium, the tungsten recovery is satisfactory; if the reverse is the case, it will be lower (Exps. 2 to 4). If, however, the amount of tungsten is very small, there appears to be no marked difference in the collecting power of the two earth acids (Exps. 11, 12).

The effect of some important mineral associates of the earth acids upon the tungsten recovery was studied in Exps. 6 to 10. They are the elements which have been shown to affect the precipitation of the earth acids (§ 25, 5 to 8). Thus, in Exp. 9, uranium caused a shortage in the weight of HP and in the tungsten recovery. Exp. 10 simulates the case of a tantalum-free titanoniobate mineral. The amount of tungstic oxide

¹ (1) *Induced Ammonia Precipitation*. Ferric hydroxide precipitated by ammonia acts as a collector of small quantities of tungstic acid (*cf.* Hillebrand and Lundell, *op. cit.*, 551). We proved that other hydroxide precipitates act like ferric hydroxide, titania being an efficient collector, uranic oxide, yttria and alumina indifferent ones.

(2) *Double Tartaric Hydrolysis*. The first hydrolysis precipitate, HP^1 , was treated by the magnesia method, yielding a precipitate, MP , consisting of the tungsten-free earth acids, and a filtrate from which the major tungsten fraction was recovered by precipitation with tannin and cinchonine. The filtrate from HP^1 was boiled down with sulphuric and nitric acids for the destruction of the tartaric acid; the liquid was transferred to a silica crucible and converted by evaporation into the original bisulphate melt, with which the ignited MP was fused. The product was dissolved in tartaric acid and the solution again hydrolysed, the precipitate, HP^2 , being treated as HP^1 for the recovery of the minor tungsten fraction.

For full details the original paper (XXXI.) should be consulted.

taken in Exps. 1 to 10—about 0.015 g.—was adopted as representing the recorded maximum content, 3 per cent., in 0.5 g. of mineral.

Exp.	G. taken.			HP.	WO ₃ in HP.	WO ₃ Error.
	M ₂ O ₅ .	WO ₃ .	Other Oxides.			
1	Ta ₂ O ₅ 0.2052	0.0145	—	0.2191	0.0142	— 0.0003
2	Ta ₂ O ₅ 0.1532	0.0158	—	0.2201	0.0154	— 0.0004
	Nb ₂ O ₅ 0.0519					
3	Ta ₂ O ₅ 0.1084	0.0160	—	0.2278	0.0148	— 0.0012
	Nb ₂ O ₅ 0.1073					
4	Ta ₂ O ₅ 0.0567	0.0140	—	0.2174	0.0132	— 0.0008
	Nb ₂ O ₅ 0.1534					
5	Nb ₂ O ₅ 0.2056	0.0151	—	0.2120	0.0128	— 0.0023
6	Ta ₂ O ₅ 0.1044	0.0170	TiO ₂ 0.0546	0.2351	0.0157	— 0.0013
	Nb ₂ O ₅ 0.1073					
7	Ta ₂ O ₅ 0.1064	0.0153	ZrO ₂ 0.0531	0.2377	0.0145	— 0.0008
	Nb ₂ O ₅ 0.1020					
8	Ta ₂ O ₅ 0.1056	0.0170	ThO ₂ 0.0544	0.2306	0.0162	— 0.0008
	Nb ₂ O ₅ 0.1020					
9	Ta ₂ O ₅ 0.1061	0.0192	U ₃ O ₈ 0.0555	0.2029	0.0172	— 0.0020
	Nb ₂ O ₅ 0.1030					
10	Nb ₂ O ₅ 0.1034	0.0184	TiO ₂ 0.1017	0.1308	0.0165	— 0.0019
11	Ta ₂ O ₅ 0.2031	0.0034	—	0.2069	0.0031	— 0.0003
12	Nb ₂ O ₅ 0.2032	0.0027	—	0.1975	0.0026	— 0.0001

As regards the application of a correction factor, the number of qualitative and quantitative variables presented by earth-acid minerals (apart from the personal equation) is too great for an exhaustive investigation by means of synthetic oxide mixtures. We recommend, therefore, that the factor be determined in each case as set out below. The analyst may thus compile a set of corrections applicable to his technique.

As for the *minor tungsten fraction*, it may safely be disregarded in the subsequent operations. In the more usual case of low tungsten contents (Exps. 11, 12), it should be negligible.

Procedure. The mineral (0.5 g.) is fused with bisulphate (3 g.), and the melt is dissolved in a solution of 3 g. of tartaric acid (§ 20). The solution is treated with hydrogen sulphide and filtered (§ 23), and the filtrate (not more than 150 ml.) is precipitated by three minutes' boiling with 25 ml. of strong hydrochloric acid (§ 25). The precipitate, *HP*, is collected and treated by the magnesia method (§ 38), and the tungstic oxide is purified by fusion with sodium hydroxide (§ 39).

For the determination of the correction factor, a synthetic oxide mixture should be put through the same process under identical conditions, the error in the tungstic-oxide recovery being added to the value obtained in the analysis of the mineral. This mixture should be made up of exactly the same quantities of the oxides of tantalum, niobium, uranium, titanium, zirconium, and

thorium as those obtained, *plus* a little (0.3 to 2 mg.) more tungstic oxide than that found in the analysis of the mineral. This excess is judged by comparison of the mineral constituents with those of the synthetic oxide mixtures given in the above table.

If the operator has no pure oxides at his disposal, recourse may be had to the products of his analysis. The precipitation of the metallic acids should be carried out in a small bulk of solution, and if the filtrate and washings from the insoluble *plus* hydrogen sulphide precipitate exceed 150 ml., the liquid should be concentrated by evaporation. Bisulphate, sulphuric and tartaric acid should be kept at a minimum, hence a second bisulphate fusion of the insoluble fraction should be avoided, if possible, by thorough decomposition in the first fusion, and expulsion of the bulk of the free acid. The wash-liquor for the hydrogen-sulphide precipitate need not contain more than a few drops of sulphuric acid.

In our experiments (1 to 12, *supra*), the tungsten determinations in *HP* by the magnesia method were made in a single treatment (*cf.* § 38), the double treatment producing no appreciable increase in the tungsten recovery. Identical treatment of synthetic oxide mixture and mineral will compensate for low results due to omission of the double treatment, or to other sources of error.

SPECIAL METHODS

§ 41. Separation of the Earth Acids from Tungstic Acid by the Sodium-chloride Method

For simple earth-acid minerals practically free from zirconium, thorium, and uranium, and containing less than 0.5 per cent. of titania (*e.g.*, tantalite, columbite), the following process may be used.

The major and the minor earth-acid fractions (*IIP*, § 25, and *TP*, § 28, respectively) are ignited in a platinum crucible, weighed as a check, and fused with potassium carbonate (§ 1). Lixiviation, precipitation of the sodium salts, and bicarbonate hydrolysis of the filtrate are carried out as in §§ 1 to 3; the tungsten in the filtrate from the small bicarbonate precipitate is determined by tannin and cinchonine (§ 37).

The sodium-chloride method, while providing a separation of the earth acids from tungsten, permits of a rapid approximate volumetric determination of tantalum and niobium. Operators

not too familiar with the tannin separation of the two elements (Chapter XI) will consider this an advantage, as they will obtain a preliminary approximation of the tantalum and niobium while separating them from tungsten. The titration and recovery of the pentoxides is fully described in § 5, while directions for the alternative gravimetric determination are given in § 4.

Schoeller and Jahn (VIII.) report the following results of their test separations of tungsten from tantalum and niobium by the sodium-chloride method. Experiments 1 to 3 were made with tantalic oxide, Exps. 4 to 6 with niobic oxide, and Exps. 7 to 10 with mixed pentoxides ($61.4 \text{ Ta}_2\text{O}_5 : 38.6 \text{ Nb}_2\text{O}_5$). It will be seen that the best results were secured with the mixed pentoxides (P^1 represents the pentoxide fraction precipitated by sodium chloride, and P^2 the pentoxide fraction precipitated by bicarbonate hydrolysis).

Exp.	G. taken		P^1	P^2	G. found		Error	
	M_2O_5	WO_3			M_2O_5	WO_3	M_2O_5	WO_3
1	0.0995	0.0204	0.0970	0.0020	0.0990	0.0206	- 0.0005	+ 0.0002
2	0.1002	0.0264	0.0980	0.0016	0.0996	0.0254	- 0.0006	- 0.0010
3	0.1500	0.0543	0.1510	0.0008	0.1518	0.0536	+ 0.0018	- 0.0007
4	0.3296	0.0090	0.3282	none.	0.3282	0.0092	- 0.0014	+ 0.0002
5	0.2055	0.0421	0.2022	0.0022	0.2044	0.0424	- 0.0011	+ 0.0003
6	0.3004	0.0338	0.2976	0.0035 ¹	0.3011	0.0334	+ 0.0007	- 0.0004
7	0.4772	0.0380	0.4760	0.0015	0.4775	0.0376	+ 0.0003	- 0.0004
8	0.3128	0.0255	0.3106	0.0024	0.3130	0.0256	+ 0.0002	+ 0.0001
9	0.2237	0.0475	0.2227	0.0016	0.2243	0.0478	+ 0.0006	+ 0.0003
10	0.3221	0.0353	0.3188	0.0028	0.3216	0.0349	- 0.0005	- 0.0004

In the same paper, Schoeller and Jahn criticise the published methods for the separation of tungsten from tantalum and niobium. The method of Berzelius (extraction of the hydrolysis precipitate with ammonium sulphide or hydroxide) is a typical process based on selective solution of a constituent of a complex precipitate, and therefore wrong in principle (Chapter II, 4). Rose's method (fusion of the ignited hydrolysis precipitate with soda and sulphur) has been criticised by several investigators as giving erratic results. If the fusion is conducted at low temperature, tungsten (and tin also) is not extracted completely; at higher temperatures, tantalum and niobium are rendered more or less soluble.

When a solution containing potassium tungstate, niobate, and tantalate is boiled with ammonium nitrate, the earth acids are said to be precipitated. We investigated this reaction, and found that potassium tantalate is quantitatively decomposed, the precipitated tantalic acid occluding a large amount of tungstic acid; on the other hand, a solution of potassium niobate is not precipitated. The deportment of the mixed earth acids

¹ Includes a little Nb_2O_5 obtained by purification of WO_3 (§ 39).

§ 41 TITANIA FROM TUNGSTIC OXIDE

depends on their relative proportions, as shown by the following experiments :

	G. taken.			Ppt.	Ta ₂ O ₅ Nb ₂ O ₅	Deposiment.
	Ta ₂ O ₅ .	Nb ₂ O ₅ .	Sum.			
1	0·1026	0·0220	0·1246	0·1236	5 : 1	as Ta ₂ O ₅
2	0·0803	0·0420	0·1223	0·1208	2 : 1	„
3	0·0610	0·0612	0·1222	0·1200	1 : 1	„
4	0·0408	0·0795	0·1203	0·0856	1 : 2	intermediate
5	0·0212	0·1084	0·1296	0·0026	1 : 5	as Nb ₂ O ₅

The reaction is of no value as a separation procedure. Fuller experimental details are given in the original paper (VIII.).

§ 42. Separation of Titania from Tungstic Oxide

Even outside the domain of earth-acid analysis, no reliable method for this separation appears to have been available. Such is the opinion of Powell, Schoeller and Jahn (XXIX.), who have investigated the subject. According to statements found in the literature,¹ fusion with alkalis or with bisulphate, followed by extraction with water, achieve the object in view. In the former case the tungsten is obtained in the filtrate, while titania remains insoluble ; in the latter case, the tungsten is said to remain in the insoluble residue, the titanium passing into the filtrate as sulphate.

We found the process based upon bisulphate fusion to be entirely useless. In Exp. 1 below, a pyrosulphate melt of the mixed oxides dissolved to a perfectly clear solution in 5 per cent. sulphuric acid ; in Exp. 2, the cloudy aqueous extract of the bisulphate melt cleared completely on warming, and remained clear while boiling. These tests dispose of the bisulphate method as a means for separating tungsten from titanium.

Exp.	G. taken.		WO ₃ found.	Error.
	WO ₃ .	TiO ₂ .		
1	0·0224	0·2028	<i>nil</i>	
2	0·0546	none	<i>nil</i>	
3	0·0205	0·2010	0·0126	— 0·0079
4	0·0212	2·2043	0·0130	— 0·0082

The case is analogous to that of titania in association with the earth acids, which undergo "loss of individuality" when associated with sufficient titania (Chapter II, 9) ; Exp. 2, however, shows that, even by itself, tungstic oxide does not remain insoluble after bisulphate fusion. No doubt, if present in larger amounts, it would be partly precipitated.

¹ *E.g.*, Bull. 212, U.S. Bureau of Mines, 1923, p. 8.

Sodium carbonate fusion followed by extraction of the melt with water (Exp. 3) or half-saturated sodium chloride solution (Exp. 4) resulted in a negative tungsten error of about 40 per cent., and the titania residue gave a positive reaction for tungsten. Re-treatment of the titania residue by the same process did not recommend itself, in view of the very imperfect separation achieved in the first fusion. Satisfactory results were, however, obtained by extraction of the sodium-carbonate melt with sodium hydroxide solution of fairly high concentration. The procedure is as follows :

Procedure. The mixed oxides (about 0.25 g.) are fused with 3 g. of sodium carbonate in a platinum crucible over a Teclu burner for twenty minutes or until the fused mass is clear. The cold crucible is transferred to a nickel dish containing a solution of 10 g. of sodium hydroxide in 50 ml. of water. The covered dish is kept on a steam-bath for two to three hours, the water lost by evaporation being replaced. The crucible is cleaned and rinsed with 50 ml. of hot water. The liquid is allowed to stand until cold or over night, and filtered. The residue, P^1 , is washed with half-saturated sodium chloride solution, and reserved.

The filtrate is treated with phenolphthalein and dilute hydrochloric acid until colourless (§ 3). The solution is heated on a steam-bath, the red colour being discharged from time to time with a drop of acid. The small precipitate, P^2 , is collected, and washed as P^1 . The tungsten in the filtrate from P^2 is determined by tannin and cinchonine (§ 37).

The filters containing P^1 and P^2 are pulped with N hydrochloric acid. The liquid is diluted to 100 ml., heated, and precipitated with ammonia; the precipitate is collected, washed with ammonium nitrate solution, and ignited to TiO_2 . Leaching (§ 13 (*d*)) is advisable if the precipitate is considerable.

The following results were obtained (XXIX.) by the above caustic-soda " method :

Exp.	G. taken.		WO_3		Earth	
	Earth.	WO_3 .	Found.	Error.	Found.	Error.
1	TiO_2 0.2030	0.0200	0.0202	+ 0.0002	0.2034	+ 0.0004
2	TiO_2 0.1685	0.0360	0.0362	+ 0.0002	0.1686	+ 0.0001
3	TiO_2 0.2387	0.0061	0.0056	- 0.0005	0.2386	- 0.0001
4	Nb_2O_5 0.2753	0.0156	0.0158	+ 0.0002	0.2742	- 0.0011
5	Ta_2O_5 0.2271	0.0206	0.0208	+ 0.0002	0.2276	+ 0.0005

The less complete tungsten recovery in Exp. 3 is ascribed to the use of caustic soda of half the strength specified above.

§ 42 TUNGSTEN FROM VARIOUS EARTHS

Niobic oxide strongly interferes in the caustic-soda method because of the modified behaviour of titania and niobic oxide in association. Each oxide without the other remains insoluble in the treatment (see Exp. 4); but a mixture of the two in approximately equal quantities gives a considerable fraction soluble in caustic soda to a semi-colloidal solution which is not completely flocculated by bicarbonate hydrolysis :

G. taken.					
Exp. 6	$\left\{ \begin{array}{l} \text{TiO}_2 \\ \text{Nb}_2\text{O}_5 \\ \text{WO}_3 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1202 \\ 0.1244 \\ 0.0304 \end{array} \right.$	$\left\{ \begin{array}{l} P^1 \\ P^2 \text{ (contains Ti and W)} \\ \text{Tannin-cinchonine ppt.} \end{array} \right.$	$\left\{ \begin{array}{l} . \\ . \\ . \end{array} \right.$	$\left\{ \begin{array}{l} 0.1630 \\ 0.0720 \\ 0.0406 \end{array} \right.$
	Sum	0.2750	Recovery	.	0.2756
	G. taken.				
	$\left\{ \begin{array}{l} \text{TiO}_2 \\ \text{Ta}_2\text{O}_5 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1070 \\ 0.0325 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Nb}_2\text{O}_5 \\ \text{WO}_3 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1139 \\ 0.0134 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Tannin-cinchonine} \\ \text{ppt.} \end{array} \right.$

Hence the magnesia method (§ 38) must be used for separations of tungstic oxide from mixtures of earth acid and titania.

§ 43. Separation of Tungstic Oxide from Zirconia, Thoria, Rare Earths, Beryllia, Ferric Oxide

The mixed oxides are fused with sodium or potassium carbonate in a platinum crucible. If zirconia (thoria) preponderates, a high proportion of flux (3 to 6 g. for 0.1 to 0.3 g. of oxide) should be used, and the fusion continued for an hour over a Teclu or Méker burner. If tungsten preponderates (*e.g.*, in the examination of impure tungstic oxide) 0.5 g. or more of the oxide may be fused with 4 to 5 g. of flux for fifteen minutes. The cooled melt is extracted with hot water; a thin cream of filter pulp is stirred into the turbid liquid, which is filtered through close-textured paper containing a pad of pulp pressed into its apex. The precipitate is collected and washed with a 2 per cent. solution of alkali carbonate; it is returned to the beaker with the filter, which is then pulped with hot water. This is acidified and made slightly ammoniacal. The precipitate is collected, washed with water containing ammonium nitrate, ignited wet, and weighed. The tungsten is determined in the clear filtrate as usual (§ 37). The separation is complete in one operation.

Zirconia. Fusion with sodium carbonate and extraction of the melt with caustic soda (§ 42) was tried in the separation of tungstic oxide from zirconia (XXIX.), with the rather surprising result that the method does not answer in this case (Exps. 1, 2 below). The low zirconia and high tungsten result must be due to incomplete hydrolysis, in the strongly alkaline medium, of some of the sodium zirconate present in the melt; the small amount of zirconia which thus accompanies the tungsten into the alkaline filtrate is not precipitated therefrom by bicarbonate hydrolysis, and most of this soluble fraction becomes occluded in the tannin-

cinchonine precipitate. This inference was confirmed by tests 3 and 4, in which the oxides were fused with alkali carbonate, and the melt was extracted with hot water only instead of caustic soda: the recovered tungstic oxide was free from zirconia.

Exp.	G. taken		WO ₃ .		ZrO ₂ .	
	ZrO ₂ .	WO ₃ .	Found.	Error.	Found.	Error.
1	0.2224	0.0334	0.0369	+ 0.0035	0.2175	- 0.0049
2	0.2000	0.0342	0.0358	+ 0.0016	0.1960	- 0.0040
3	0.2045	0.0311	0.0306	- 0.0005	Flux: Na ₂ CO ₃	
4	0.2056	0.0328	0.0328	0.0000	Flux: K ₂ CO ₃	

Thoria, Rare Earths, Beryllia, Ferric Oxide. The separation of tungstic oxide from these oxides was studied by Wunder and Schapiro,¹ who used substantially the same process as the one here described. In order to obtain a clear filtrate, they use a close-textured paper, and recommend addition of 1 g. of solid sodium (potassium) carbonate to the turbid liquor prior to filtration. It is difficult to see precisely what effect the addition of solid alkali carbonate to the carbonate solution may have on the filtering properties of the insoluble oxides. Wunder and Schapiro do not mention the use of filter pulp in the filtration, an expedient we strongly recommend for the retention of the finely divided residue.

¹ *Ann. Chim. Anal.*, 1912, 17, 323; 1913, 18, 257.

CHAPTER VIII

THE SEPARATION OF THORIA AND THE RARE EARTHS FROM OTHER EARTHS

Introduction

WHILE the earths composing the tartaric hydrolysis precipitate are being freed from tungstic oxide (Chapter VII), those contained in the ammonia precipitate will be resolved into two groups by the application of reagents which precipitate thoria and the rare earths, but not the other constituents.

Thoria, scandia, and the rare earths (*i.e.*, the oxides of the cerium, terbium, and yttrium groups) share the property of forming insoluble fluorides and oxalates, and it is on the precipitation of these compounds that the separation methods discussed below are based. The fluoride method is the subject of § 44, while the oxalate method is discussed in § 45. It is understood that the directions given in this chapter apply to minerals poor in rare earths, which are analysed by the tartaric-acid method. For minerals containing rare earths as major constituents, the hydrofluoric-acid method (Chapter VI) should be used.

§ 44. The Fluoride Method

The description of the procedure given in this paragraph is based on that given by Hillebrand and Lundell.¹

Procedure. The ammonia precipitate obtained in § 29 (Chapter V) is rinsed into a platinum dish; the filter paper is washed with dilute hydrofluoric acid, then with water, ignited, and the ash is added to the solution. This is evaporated almost to dryness, the residue is taken up in water and a few drops of hydrofluoric acid, and the liquid is digested hot for some time. After cooling, it is filtered (rubber funnel) into a platinum dish, and the precipitate is washed with water containing a little hydrofluoric acid.

The fluoride precipitate is rinsed into a platinum dish; the paper is ignited and the ash is added to the precipitate. The suspension is evaporated with 1 to 2 ml. of sulphuric acid, which is completely expelled by heating in an air-bath. The residual sulphates are dissolved in cold water, and the hot solution is precipitated with oxalic acid. After standing for some time,

¹ *Op. cit.*, p. 436.

preferably overnight, the precipitate is collected, washed with 1 per cent. oxalic acid, cautiously ignited, and weighed.

The filtrate from the fluoride precipitate is evaporated with 10 ml. of sulphuric acid (1 : 1), etc., as described in § 48, (a) (1) (Chapter IX).

§ 45. The Oxalate Method

The alternative to the fluoride separation consists in precipitating the rare earths and thoria as oxalates. According to Hillebrand and Lundell,¹ the fluoride method "in general gives more complete precipitation." Whilst I do not claim to speak with the same authority on the analytical chemistry of the rare earths as I do on that of the earth acids, I hold that the oxalate procedure about to be described presents advantages over the fluoride method, besides being reasonably accurate. The oxalate method is very simple and rapid, can be carried out in glass vessels, and the filtrate from the oxalate precipitate is ready for the next operation (Chapter IX).

The usual procedure consists in dissolving the ammonia precipitate in hydrochloric acid, and removing the excess acid by evaporation short of complete dryness. The residue is moistened with water and treated with a few drops of hydrochloric acid if necessary, but not more than necessary to produce a clear solution. This is diluted with a little hot water and precipitated with a large excess of oxalic acid solution.

This process, when applied in the tartaric-acid method, presents the difficulty that the ammonia precipitate, after evaporation with hydrochloric acid, is likely to give a turbid solution, because it contains the minor earth-acid fraction. To overcome this difficulty I propose extracting a bisulphate melt of the ammonia precipitate with oxalic acid solution. A procedure of this kind was first suggested by Pied,² whose paper deals with the precipitation of the earth acids by cupferron from oxalo-tartaric solution after the removal of iron as sulphide. The paper concludes with a seven-line paragraph containing the following passage in literal translation :

"I have ascertained that the oxalic solution [of the earth acids] can be obtained by direct treatment of the fused mass obtained from the calcined oxides and many minerals by an attack with pyrosulphate. The rare earths and thorium do not hinder the dissolution ; they form a crystalline precipitate, the size of which allows of their evaluation in the mineral."

As no numerical data are adduced in Pied's paper, Schoeller and Waterhouse (XXVIII.) undertook a quantitative investigation of its application in the separation of the rare earths from the earth acids. The test separations from substantial amounts of earth acid gave indifferent results. Niobic oxide was readily soluble in the reagents used, but tantalum oxide contaminated the residual oxalates to such an extent that the ignited precipitates contained more pentoxide than rare earth. We came to the conclusion that the method proposed by Pied is not suitable for quantitative separations of amounts exceeding a few centigrams of earth acid, rare earths, and thoria. Our conclusion was

¹ *Op. cit.*, p. 435.

² *Compt. Rend.*, 1924, 179, 897 ; *Analyst*, 1925, 50, 36.

verified experimentally, the method working satisfactorily with small quantities of pentoxides and rare earths (§ 47, Exps. 1 to 5). This condition is fulfilled by the ammonia precipitate obtained in the analysis of minerals poor in rare earths after the removal of the major earth-acid fraction by tartaric hydrolysis. The major constituents of the ammonia precipitate (*e.g.*, titania, zirconia, uranic oxide) do not appear to interfere in Pied's method, as proved by my hitherto unpublished tests :

Exp.	G. added					
	TiO ₂ .	ZrO ₂ .	U ₂ O ₅ .	G. taken.	Found.	Error.
1	0.0560	0.0512	0.0524	ThO ₂ 0.0100	0.0099	- 0.0001
2	0.0510	0.0512	0.0591	CeO ₂ 0.0102	0.0103	+ 0.0001
3	0.0508	0.0532	0.0560	Y ₂ O ₃ 0.0106	0.0105	- 0.0001

Procedure. The ammonia precipitate obtained in § 29 (Chapter V) is ignited in a tared silica crucible, and weighed as a check. It is then fused with 2 g. of *sodium* bisulphate. The potassium salt should not be used, as it forms sparingly soluble potassium quadroxalate at the next stage. When cold, the crucible is filled with hot 5 per cent. oxalic acid solution, and warmed until the cake is detached. The contents of the crucible are transferred to a 150-ml. beaker, and the crucible is rinsed with more reagent (about 50 ml. in all) and discarded. The solution is kept on a steam-bath for fifteen minutes, and set aside in the cold for some hours, preferably overnight. The precipitate is collected on a 7-cm. filter containing a pad of filter pulp pressed into its apex, and washed with 1 per cent. oxalic acid solution. (Treatment of filtrate : see Chapter IX, § 48, (a) (2).)

For the determination of the sum of thorium and rare earths (if more than 0.02 g.) I prefer to convert the oxalates into oxides by the following process, the oxalate precipitate being liable to contain a little adsorbed soda. The filter containing precipitate and pulp is placed in a 400-ml. beaker, dissolved in about 5 ml. of strong sulphuric acid, and the organic matter is destroyed by heating with nitric acid (§ 10). The excess of acid is driven off, the residue is taken up in cold water, and the earths are precipitated with ammonia and tannin (§ 87, c). The precipitate is collected, washed with dilute ammonium nitrate solution, ignited in a tared silica crucible, and weighed.

§ 46. Examination of the Rare-earth Fraction

It is not intended here to give a description of the more familiar standard methods for the examination of the rare-earth fraction ; they have already been referred to in § 32. The following notes are intended

as an aid to the characterisation of the earths contained in the oxalate precipitate.

Thoria and Scandia. Amongst earth-acid minerals, only wiikite (*q.v.*, Chapter III) has so far been proved to contain more than a fraction of 1 per cent. of scandia, while euxenite, which appears to come next as regards the scandia content, may carry 0.1 to 0.2 per cent. of this earth. Spectrographic traces are found in many earth-acid minerals.

Scandia may be precipitated as hydroxide, fluoride, and oxalate by the same processes as thoria and the rare earths. In the thiosulphate method for the separation of thoria from the rare earths, scandia accompanies the thoria. The weighed precipitate may be tested by a wet method, consisting in fusion with bisulphate, precipitation with ammonia, solution in hydrochloric acid, and neutralisation of the solution with ammonia. One drop of hydrochloric acid (1 : 1) is added, and the liquid (50 ml.) is poured drop by drop into a boiling 20 per cent. ammonium tartrate solution (50 ml.). Boiling is continued for forty minutes, a few ml. of ammonia being added from time to time. The solution is allowed to cool, and filtered. The crystalline precipitate is washed with cold 5 per cent. ammonium tartrate solution, ignited wet in a platinum crucible, and weighed as Sc_2O_3 . The procedure is not strictly quantitative. The best process is spectrographic examination of the rare-earth fraction by the arc method.

Ceria Earths. The filtrate from the thiosulphate precipitate is treated with sodium hydroxide and a little hydrogen peroxide for the recovery of the rare earths. The precipitate is dissolved in hydrochloric acid, the excess of which is expelled by evaporation, and the solution is treated by the sodium-sulphate method for the separation of the cerium group (insoluble double sulphates) from the yttrium group (soluble double sulphates).

The detection and volumetric determination of cerium in the cerium group present no difficulties. Neodymia often reveals itself by the delicate pink tinge of the oxalate precipitate, especially when gathered on the filter. The most conspicuous member of the group is praseodymium, on account of the more or less intense cinnamon-brown colour which its higher oxide imparts to the ignited oxalate precipitate. In fact, the depth of colour of the crude ignited precipitate can be taken as a good guide to the relative abundance of the two main rare-earth groups in the mineral: the greater the proportion of yttria earths, the paler the precipitate. Lanthana furnishes no coloured compounds or distinctive colour reactions. Being an abundant earth, it always accompanies ceria and the didymias.

Yttria Earths. The most abundant earth is yttria, erbia coming next in order of importance. Yttria being colourless, the mixed yttria earths are colourless to pale-yellow if high in yttria, but those richer in erbia are of a deeper yellow to reddish hue.

When the percentage of yttria earths in a mineral is high, it is customary to divide the percentage of yttria earths found between yttria and "erbia, etc." This can be done by determination of the mean atomic weight, as the atomic weight of yttrium is 88.92, whilst those of the other members of the yttrium group range from $\text{Dy} = 162.5$ to $\text{Lu} = 175.0$, with a mean value of 168.7 near the atomic weight of erbium (167.64). The determination is based on that of the ratio $\text{R}_2\text{O}_3 : \text{R}_2(\text{SO}_4)_3$, conducted either synthetically (conversion of the oxides into the sulphates) or analytically (conversion of the sulphates into the oxides).

§ 46 RARE EARTHS FROM EARTH ACIDS

In either case, ignition to constant weight is of vital importance in arriving at a reliable figure.

A volumetric method, consisting in solution of the earths in 0.5 *N* sulphuric acid and determination of the excess acid by means of 0.1 *N* sodium hydroxide solution, has been worked out by Feit and Przybilla.¹ The merits and drawbacks of the various processes are discussed in Meyer and Hauser's monograph,² pp. 215-227.

SPECIAL METHOD

§ 47. Determination of Small Amounts of Rare Earths in Tantallic and Niobic Oxides

This may be effected by the following procedure, based on tartaric hydrolysis, and elaborated by Schoeller and Waterhouse (XXVIII.).

Procedure. The oxide (0.5 g.) is fused with 6 g. of potassium bisulphate in a silica crucible, and the product is dissolved in 60 ml. of 10 per cent. tartaric acid solution (§ 8). The liquid, diluted to 400 ml., is boiled with 50 ml. of strong hydrochloric acid for three minutes. The precipitate is left to settle, collected under slight suction on a 12.5 cm. paper containing a pad of filter pulp, returned to the beaker, stirred up with acidulated water, again collected, washed, and discarded.

The filtrate contains the minor earth-acid fraction and the whole of the rare earths present. It is made ammoniacal, heated to boiling, and treated with 10 g. of ammonium acetate and a fresh solution of 0.7 g. of tannin. The rare earths and earth acids are precipitated, the latter acting as a collector for minute amounts of the former. The precipitate is filtered off, washed with ammonium nitrate solution containing a little tannin and ammonia, and ignited in a silica crucible.

If the rare-earth content is very low, several 0.5 g. portions should be worked up separately. The tannin precipitates are combined, ignited, fused with bisulphate, the melt is dissolved in tartaric acid, and the solution is again hydrolysed with hydrochloric acid. The filtrate is treated with ammonia and tannin, the precipitate containing the rare earths from several portions.

The ignited tannin precipitate is fused with 2 g. of *sodium* bisulphate, and the melt is treated by one of the following two procedures:

(a) By Pied's process, *i.e.*, extraction with 5 per cent. oxalic acid solution, etc., as in § 45.

(b) By oxalate precipitation from tartrate solution, *i.e.*, solution

¹ *Z. anorg. Chem.*, 1905, **43**, 202; 1906, **50**, 249.

² *Op. cit.* (see Chapter I).

of the melt in tartaric acid, precipitation of the hot solution with saturated oxalic acid solution during agitation ; filtration next day, and ignition of the precipitate to oxides.

The following results are reproduced from Schoeller and Waterhouse's paper (XXVIII.). Experiments 1 to 5 were conducted according to method (a), and 6 to 11 by method (b). *TP* represents the weight of the combined minor earth-acid fraction and rare earth ; *OP* is the weight of the ignited oxalate precipitate.

Exp.	G. taken.		<i>TP.</i>	Rare Earth.	
	<i>M₂O₅.</i>	Rare Earth.		<i>OP.</i>	Error.
1	Ta ₂ O ₅ 0·2052	CeO ₂ 0·0211	0·0251	0·0200	— 0·0011
2	Nb ₂ O ₅ 0·2037	CeO ₂ 0·0220	0·0366	0·0216	— 0·0004
3	Ta ₂ O ₅ 0·2022	Y ₂ O ₃ 0·0234	0·0298	0·0225	— 0·0009
4	Nb ₂ O ₅ 0·2013	Y ₂ O ₃ 0·0217	0·0366	0·0220	+ 0·0003
5	Ta ₂ O ₅ 0·2026	Nd ₂ O ₃ 0·0207	0·0264	0·0212	+ 0·0005
6	Ta ₂ O ₅ 0·2018	CeO ₂ 0·0224	0·0274	0·0219	— 0·0005
7	Nb ₂ O ₅ 0·2010	CeO ₂ 0·0247	0·0377	0·0252	+ 0·0005
8	Ta ₂ O ₅ 0·2020	Y ₂ O ₃ 0·0234	0·0300	0·0231	— 0·0003
9	Nb ₂ O ₅ 0·2022	Y ₂ O ₃ 0·0230	0·0370	0·0235	+ 0·0005
10	Ta ₂ O ₅ 0·2048	Nd ₂ O ₃ 0·0284	0·0360	0·0272	— 0·0012
11	Nb ₂ O ₅ 0·2024	Nd ₂ O ₃ 0·0250	0·0394	0·0245	— 0·0005

The ignited rare earths should, of course, be tested for thorium. The above process effects a much better separation than the obsolete pyro-sulphate-hydrolysis method (§ 18), in which the insoluble earth-acid residue from the extraction of the bisulphate melt retains rare earths. The original paper (XXVIII.) contains experimental evidence for the quantitative precipitation of ceria and yttria by tannin and ammonia from pure acetate and from tartrate solutions, and for the non-occlusion of rare earths in the earth-acid precipitate produced by tartaric hydrolysis.

CHAPTER IX

THE SEPARATION OF THE EARTH ACIDS AND TITANIA FROM OTHER EARTHS

Introduction

THE third stage of the process outlined in the Introduction to Part II consists in the separation of the earth acids and titania from zirconia (hafnia); alumina, beryllia, and uranic oxide.

The separation of this complex mixture into two groups is effected by means of tannin, a procedure first applied by Powell and Schoeller (XVIII.) to the separation of titania from zirconia, and converted by them into a group separation (XXIII.). It is based upon the following principle :

Tannin quantitatively precipitates tantalum, niobium, and titanium from a feebly acid oxalate solution half-saturated with ammonium chloride. Zirconia (hafnia), thorium, alumina, beryllia, and uranic oxide are not precipitated under those conditions. A quantitative separation of any (or all) of the precipitable, from any (or all) of the non-precipitable, elements can thus be achieved.

Tannin, therefore, acts as a group reagent, by separating the earths into two groups :

Acid tannin group (or Group A) : Ta_2O_5 , Nb_2O_5 , TiO_2 .

Basic tannin group (or Group B) : ZrO_2 , HfO_2 , ThO_2 , Al_2O_3 , BeO , UO_3 .

The oxides of Group A are of a more *acid* nature, and are precipitated by tannin from faintly *acid* oxalate solution. The oxides of Group B are more *basic*, and are precipitated by tannin from the oxalate solution when it is made ammoniacal.

This remarkable process is based on a combination of three factors, namely, the more pronounced differentiation in chemical behaviour between the two groups, brought about by the conversion of the earths into their oxalo-complexes ; the high concentration of the solution in ammonium chloride, which is essential for the complete flocculation of Group A (particularly the niobium) precipitate in the slightly acid solution ; and the characteristic colour of the tannin complexes of Group A (Chapter II, 9), thanks to which the progress of the separation is controlled by the observation of colour changes. A quantitative separation of

Group A from Group B is brought about by double (§ 49) or fractional (§ 50) precipitation.

For the separation of large quantities of earth acid from zirconia, fusion with potassium carbonate is a convenient method (§ 52).

§ 48. Preparation of the Solution

(a) *In the Tartaric-acid Method* (Chapter V.). The elements to be separated are contained in two fractions resulting from the preceding manipulations. The two fractions are first combined as follows.

The ammonia precipitate may be freed from thoria and rare earths either by the fluoride (§ 44), or the oxalate (§ 45) method.

(1) If the *fluoride method* was used, the filtrate from the insoluble fluorides is evaporated with 10 ml. of sulphuric acid (1 : 1) in a platinum dish or crucible until strong white fumes are given off; the mass is left to cool, and cautiously diluted with water, the sides of the vessel being washed down. The liquid is evaporated once more, left to fume freely for a while, and again cooled. The ignited tannin precipitate of crude earth acids recovered from the separation of tungsten by the magnesia method (§ 38) is now added, together with 3 to 4 g. of potassium bisulphate (pure crystallised potassium sulphate may be used), and the mixture is heated until the excess of sulphuric acid is expelled and a clear bisulphate melt results. This is dissolved in 75 to 100 ml. of saturated ammonium oxalate solution.

(2) If the *oxalate method* was used, the filtrate from the oxalates of thoria and the rare earths, after approximate neutralisation with ammonia (and addition of some more saturated ammonium oxalate solution if necessary), is used for the solution of the bisulphate melt of the ignited tannin precipitate of the earth acids recovered from the magnesia method (see (1) above).

(b) In J. Lawrence Smith's hydrofluoric-acid method, the filtrate from the rare-earth fluorides is treated as described in § 33 by the following sequence of operations: expulsion of hydrofluoric acid, conversion into a bisulphate melt, solution in tartaric acid, precipitation of the earth acids by tartaric hydrolysis, determination of tungstic oxide in *HP*, and recovery of the earth acids by tannin (§ 38); fusion of the earth-acid precipitate with the bisulphate melt obtained after destruction of the tartaric acid in the filtrate from *HP*. This melt being free from thoria and rare earths, is dissolved in ammonium oxalate solution as under (a) (1) above.

§ 49. Separation by Double Precipitation

The separation will be considered under two heads: double precipitation (this §) for cases in which Group B is low in uranium, or preponderates over Group A; and fractional precipitation (§ 50), recommended for substantial quantities of uranium or of Group A oxides. Double precipitation is a simpler operation than fractional precipitation, but the complete precipitation of Group A is more difficult to observe if the precipitate is large; hence precipitation in two fractions is safer, though an operator familiar with the procedure and the material under treatment may elect to use double precipitation even in such cases.

Double Precipitation. The whole of Group A is precipitated in one operation, and the precipitate is re-treated by the same procedure.

Neutralisation. The boiling oxalate solution (150 to 200 ml. for 0.2 to 0.4 g. of oxides) is well stirred and neutralised with *N* ammonia added drop by drop (a burette is convenient) to the appearance of a faint cloudiness, which is immediately removed with a drop or two of dilute hydrochloric acid. At this point a small bit of blue litmus paper dropped into the solution should turn red. The solution is diluted with an equal bulk of saturated ammonium chloride solution. A stock solution containing a little ammonium oxalate (to remove traces of lime) and filtered before use is convenient.

First Precipitation. The boiling solution is treated with fresh 5 per cent. tannin solution added drop by drop from a burette during continuous agitation. The amount of tannin required for the complete precipitation of Group A is ten to twelve times the weight of the oxides, niobic and titanitic oxides requiring more precipitant than does tantalic oxide. The beaker is left on a hot plate, when the flocculent precipitate will gather into clouds, leaving the liquid clear. If the latter shows any orange tint, an insufficiency of tannin is indicated, and a further cautious addition of the reagent should be made. If, however, the clear liquid is colourless or of a pale straw-yellow tint, the precipitation of Group A is probably complete. After half an hour's digestion on a hot plate, the precipitate, P^1 , is collected under moderate suction on one or two 12.5-cm. filters containing a little filter pulp (§ 13 (b)), returned to the beaker for washing with a solution of ammonium chloride and oxalate (5 : 1 per cent.), and ignited wet in a silica crucible.

Test for Complete Precipitation. The filtrate from P^1 is again boiled, treated with about 0.1 g. of tannin, and titrated with *N*

ammonia until a precipitate is formed. If this is dirty-grey (Zr, Al, Be) to brown (U), and readily soluble in a little dilute hydrochloric acid, complete precipitation of Group A has been achieved; if pale orange, titanium or niobium is still present (the precipitation of tantalum is complete at a higher acidity); a further small addition of tannin and ammonia is made, and the precipitate, P^{1a} , is collected as P^1 , being ignited in the same crucible. The filtrate from P^{1a} should again be tested as before.

The elements of Group B are recovered from the filtrate as described in § 51.

Second Precipitation. The precipitate P^1 (or $P^1 + P^{1a}$) is weighed as a check, fused with bisulphate, and the melt is dissolved in ammonium oxalate solution as before, small quantities of silica or grit being filtered off and washed with hot water. The filtrate is again neutralised as above, diluted with an equal bulk of saturated ammonium chloride solution, and precipitated while boiling with twelve times as much tannin as the oxides present. The precipitate, P^2 , is collected, washed, and ignited as P^1 in a tared porcelain crucible; it should be leached (§ 13 (d)) before being finally weighed as $(Ta, Nb)_2O_5 + TiO_2$.

The filtrate from P^2 should be tested for complete precipitation of Group A (*supra*); it is worked up for small amounts of Group B oxides according to § 51.

§ 50. Separation by Fractional Precipitation

(For oxides high in uranium, or large amounts of Group A oxides.) If the addition of tannin to the solution is restricted to about eight times the weight of Group A oxides assumed to be present, the recovery of Group A will be more or less incomplete, but the major fraction P^1 will be very pure, and its removal by filtration facilitates the completion of the operation, viz., precipitation of the balance of Group A in the form of a smaller, probably less pure fraction P^{1a} .

Major Fraction (P^1). Neutralisation of the boiling solution is effected as in § 49, followed by addition of saturated ammonium chloride solution and dropwise addition of a 5 per cent. tannin solution, etc. The whole operation is exactly the same as the first precipitation in the preceding paragraph, except for the smaller addition of tannin. The precipitate P^1 is ignited in a tared silica crucible.

Minor Fraction (P^{1a}). The filtrate from P^1 is concentrated while the precipitate is being washed. The washings also are concentrated if necessary until the combined bulk is substantially the same as before filtration of P^1 . The boiling liquid is treated

with about one-half as much tannin solution as before, stirred, and titrated with *N* ammonia until the orange precipitate, P^{1a} , shows signs of discoloration which, if pronounced, can be removed with a drop of dilute hydrochloric acid. The precipitate is left to settle on a hot plate, collected and washed as before, and ignited in the crucible containing P^1 . The filtrate from P^{1a} must be tested for complete precipitation of Group A (§ 49).

Testing the Precipitate for Purity. The combined fractions $P^1 + P^{1a}$ are tested for purity by re-precipitation under exactly the same conditions as the *second precipitation*, § 49. The ignited precipitate, P^2 , is leached, again ignited, and weighed as $(Ta, Nb)_2O_5 + TiO_2$.

Treatment of filtrates from P^{1a} and P^2 : see § 51.

§ 51. Recovery of Group B from the Tannin Filtrates

Whether the precipitation of Group A has been carried out by double or fractional precipitation, the members of Group B are contained in two filtrates, the major fraction in that from P^1 or P^{1a} , and the normally very small minor fraction in that from P^2 (§§ 49, 50).

Major Fraction. (a) The recovery may be effected by precipitation with tannin from ammoniacal solution. The filtrate from P^1 or P^{1a} is heated to boiling, and treated with ten times as much tannin as the oxides of Group B present, and 10 ml. of ammonia (1 : 1). After short boiling, the solution is kept on a hot plate for half an hour, then left for some hours at room temperature. The light brown to dark brown precipitate is collected (under suction if substantial), washed with 5 per cent. ammonium nitrate solution, and ignited. Its weight is almost certainly excessive, due to adsorption of salts and contamination with silica. The analysis of the precipitate is discussed in Chapter XII.

(b) If the quantity of Group B oxides is considerable, the operator may prefer to recover them by ammonia precipitation. For this purpose the filtrate is boiled down in a large flask with 100 ml. of strong nitric and 10 ml. of strong sulphuric acid for the destruction of the tannin, oxalate, and ammonium chloride. When effervescence has ceased, the liquid is transferred to a 600-ml. beaker, and the evaporation is continued until all the nitric and some of the sulphuric acid have been expelled. The acid mass is cooled, diluted with water, the liquid is filtered from a little silica, and the filtrate is heated to boiling after approximate neutralisation with ammonia. The boiling liquid is made slightly ammoniacal, and a little tannin solution is added; the precipitate is mixed with filter pulp, collected, washed with

ammonium nitrate solution, ignited, and weighed as a check (Analysis of precipitate : Chapter XII).

Minor Fraction. This is normally so small as to yield a tannin precipitate which can be collected by simple filtration on loose-textured paper when treated as described under (a) above for the major fraction. The small precipitate is ignited and added to the major fraction.

The tables below give representative test separations of Group A from Group B, the separation of one member of the former from one of the latter being shown in Table I., and the resolution of more complex mixtures in Table II.

Table I. (Analyses 1 to 4 by Powell and Schoeller (XVIII.); 5 to 7 by Schoeller and Webb (XXV.); 8 to 10 by Schoeller and Webb (XXX.); 11 to 16 by Schoeller and Powell (XXIII.)). The entries under P^1 give the gross weight of the first precipitate or major fraction, recorded as a guide for the progress of the separation. Where no entry has been made in the next column under P^{1a} , the whole of Group A was precipitated as P^1 , which was accordingly re-treated as in § 49. The P^2 thus obtained was purified and weighed (§ 50), the result being entered under *Final P^2* . Fractional precipitation (§ 50) is shown by a recovery under P^{1a} ; in Exps. 5 to 7, however, the weights given under P^{1a} are those of precipitates obtained by a re-treatment of the actual P^{1a} , a mode of working recommended for separations involving large amounts of uranium. This element, unlike Zr, Al, Be, Th, furnishes a deeply coloured tannin complex which, when about to flocculate near the neutral point, imparts a brown tint to the solution. Any such interference is overcome by the precipitation of the balance of Group A as an intermediate fraction, which is re-treated before being added to P^1 .

TABLE I
Binary Mixtures

Exp.	G. taken.		Group A.				Group B.	
	Group A.	Group B.	P^1 .	P^{1a} .	Final P^2 .	Error.	Recovery.	Error.
1	TiO ₂ 0'0210	ZrO ₂ 0'2006	0'0245	—	0'0214	+ 0'0001	0'2012	+ 0'0006
2	" 0'0516	" 0'2073	0'0572	—	0'0522	+ 0'0006	0'2063	— 0'0010
3	" 0'0084	" 0'2001	0'0092	—	0'0086	+ 0'0002	0'1993	— 0'0008
4	" 0'0538	" 0'1306	0'0690	—	0'0534	— 0'0004	0'1295	— 0'0001
5	Ta ₂ O ₅ 0'1045	U ₃ O ₈ 0'1104	0'0040	0'0039	0'1054	+ 0'0009	0'1013	+ 0'0002
6	Nb ₂ O ₅ 0'1383	" 0'1104	0'1378	0'0039	0'1385	+ 0'0003	0'1099	— 0'0005
7	TiO ₂ 0'1140	" 0'1107	0'1125	0'0044	0'1151	+ 0'0005	0'1113	+ 0'0006
8	" 0'0183	BeO 0'0455	—	—	0'0186	+ 0'0003	0'0449	— 0'0006
9	Ta ₂ O ₅ 0'1132	" 0'0538	—	—	0'1132	0'0000	0'0534	— 0'0004
10	Nb ₂ O ₅ 0'1335	" 0'0330	—	—	0'1338	— 0'0007	0'0533	+ 0'0003
11	Ta ₂ O ₅ 0'1048	ZrO ₂ 0'1014	0'1072	—	0'1053	+ 0'0005	1'2	†
12	Nb ₂ O ₅ 0'1001	" 0'1055	0'1054	0'0052	0'1003	— 0'0002	1'3	
13	Ta ₂ O ₅ 0'1051	ThO ₂ 0'1042	0'1038	0'0017	0'1042	— 0'0009	1'0	
14	Nb ₂ O ₅ 0'1066	" 0'1028	0'0999	0'0077	0'1066	0'0000	0'8	
15	TiO ₂ 0'0479	" 0'1068	—	—	0'0484	+ 0'0005	0'8	
16	" 0'0532	Al ₂ O ₃ 0'2357	—	—	0'0528	— 0'0004	0'8	

* Not weighed.

† g. tannin used for precipitating P^1 .

Table II. (Analyses 17 to 20, by Schoeller and Powell (XXIII.) ; 21, 22, by Schoeller and Webb (XXV.) ; 23, by Schoeller and Webb (XXX.)). For greater simplicity, the quantities of Ta_2O_5 and Nb_2O_5 , though weighed up separately, have been added together and entered as M_2O_5 under Group A. The column headed " Tannin " shows the weight of reagent used as precipitant for P^1 .

A substantial amount of ferric oxide was included in Exp. 22. When present in quantity, iron is a less tractable member of Group B because the inkiness of the solution at or near the neutral point obscures the more delicate colour indications which form an important feature of the process. In Exp. 22, tannin was added to the almost neutral solution until the

TABLE II
Ternary to Septenary Mixtures

Exp.	G. taken		Tannin.	Group A.			
	Group A.	Group B.		P^1	P^{1a}	Final P^2	Error.
17	M_2O_5 0.0637	ZrO_2 0.1004	1.5	0.1259	—	0.1192	+ 0.0004
	TiO_2 0.0551						
	0.1188						
18	Nb_2O_5 0.0628	ThO_2 0.0721	1.2	0.1055	0.0023	0.1059	— 0.0002
	TiO_2 0.0433						
	0.1061						
19	M_2O_5 0.1052	Al_2O_3 0.1072	2.0	0.1584	0.0056	0.1587	+ 0.0001
	TiO_2 0.0534						
	0.1586						
20	M_2O_5 0.0734	ZrO_2 0.0567	1.5	0.1152	—	0.1112	— 0.0002
	TiO_2 0.0380	ThO_2 0.0303					
	0.1114	Al_2O_3 0.0540					
21	M_2O_5 0.0950	ZrO_2 0.0371	1.0	0.1347	0.0014	0.1304	— 0.0004
	TiO_2 0.0358	ThO_2 0.0323					
	0.1308	U_3O_8 0.0383					
22	M_2O_5 0.0941	ZrO_2 0.0545	1.0	0.1370	0.0021	0.1321	— 0.0009
	TiO_2 0.0389	ThO_2 0.0384					
	0.1330	U_3O_8 0.0515					
23	M_2O_5 0.0309	BeO 0.0120	1.2			0.1329	+ 0.0001
	TiO_2 0.1019						
	0.1328						

darkening of precipitate and solution indicated incipient precipitation of iron, hence complete precipitation of Group A. The ignited P^1 , which was mottled pink, was re-treated by fractional precipitation yielding iron-free precipitates P^2 (0.1311 g.) and P^3 (0.0021 g.), which were white after ignition and gave a purified final P^3 weighing 0.1321 g.

The experiments reproduced in Tables I. and II have necessarily had to be condensed; they are given in considerable detail in the four papers quoted, which the reader is invited to study for fuller particulars.

SPECIAL METHOD

§ 52. Separation of the Earth Acids from Zirconia by Fusion with Potassium Carbonate

At an early stage of our investigations, this method, proposed by Giles,¹ was studied by Schoeller and Powell (II.) who found that it afforded a satisfactory separation of zirconium from niobium (by a single or, preferably, double fusion), but not from tantalum, the recovery of which gave a negative error of 2 to 8 mg. even after three fusions. The work was continued by Schoeller and Waterhouse (XIII.), who succeeded in completing the separation of tantalum from zirconium by applying tannin precipitation to the oxalate solution of the zirconia residue from the carbonate fusion. Their tannin procedure was the precursor of the method described in the preceding paragraphs of this chapter, the essential difference being that the older method was not carried out in half-saturated ammonium chloride solution; this gave an indifferent separation of zirconium from small quantities of niobium in absence of tantalum.

Whilst the group separation discussed in this chapter is the standard process for the separation of any or all the earths of Group A from any or all the oxides of Group B, fusion with potassium carbonate is a very useful step in the quantitative separation of small quantities of zirconia from much earth acid. If it is desired to detect or determine small amounts of zirconia in the pentoxides, the fusion conveniently removes the bulk of the latter in the form of soluble potassium salts; the tannin method, on the other hand, would involve the handling of an inconveniently large precipitate liable to occlude zirconia. The fusion method allows several g. of pentoxide to be taken for analysis (in 1-g. portions). The tannin method constitutes a most delicate test for the smallest quantities of pentoxide in zirconia, a preliminary concentration being effected into a precipitate P^1 containing the whole of the pentoxide with some zirconia.

Procedure. The mixed oxides are fused with potassium carbonate (6 parts) in a platinum crucible, and the melt is dissolved in water containing a little potassium hydroxide (§ 1). The contents of the crucible are transferred to a small beaker, and filter pulp is stirred into the turbid liquid, which is then passed through a filter containing a pulp pad pressed into its apex. Care should be taken to ensure a perfectly clear filtrate; the first

¹ *Chem. News*, 1909, 99, 1.

portion of filtrate is preferably returned to the filter. The residue is washed with 2 per cent. potassium carbonate solution; the filter is returned, pulped with water, and treated hot with a little dilute hydrochloric acid, then with a slight excess of ammonia. The precipitate is collected, washed with ammonium chloride solution, and ignited either in a platinum crucible (if it is desired to repeat the carbonate fusion, in which case the above cycle of operations is repeated), or a silica crucible.

The zirconia fraction thus obtained, still contaminated with a little pentoxide, is fused with bisulphate, and the solution of the melt in ammonium oxalate is treated as in § 49.

The difference in behaviour of Ta_2O_5 and Nb_2O_5 is shown in the following two tests by Schoeller and Powell (II.), in which the carbonate melt was leached with water without addition of potassium hydroxide :

Exp.	G. taken.	Weight of products from			Purified Oxides.	Errors.
		1st Fusion.	2nd Fusion.	3rd Fusion.		
1	Ta_2O_5 0.2509	0.2174	0.0342	0.0086	0.2476	- 0.0033
	ZrO_2 0.2534	0.3028	0.2726	0.2682	0.2588	+ 0.0054
2	Nb_2O_5 0.2520	0.2673	0.0045	—	0.2511	- 0.0009
	ZrO_2 0.2509	0.2661	0.2563	—	0.2515	+ 0.0006

The following results were obtained by Schoeller and Waterhouse (XIII.) by the combination method (*i.e.*, potassium carbonate fusion, yielding the major earth-acid fraction P^1 , and recovery of the minor fraction, P^2 , from the zirconia fraction by the tannin method) :

Exp.	G. taken.		No. of K_2CO_3 Fusions.	P^1	P^2	M_2O_5	
	M_2O_5	ZrO_2				Found.	Error.
1	Ta_2O_5 0.2400	0.2770	2	0.2366	0.0038	0.2404	+ 0.0004
2	" 0.3060	0.2030	2	0.3010	0.0046	0.3056	- 0.0004
3	" 0.1049	0.2338	1	0.0955	0.0087	0.1042	- 0.0007
4	$(Ta, Nb)_2O_5$ 0.2154	0.3160	1	0.2110	0.0049	0.2159	+ 0.0005

Potassium carbonate fusion can be applied to the separation of Ta_2O_5 , Nb_2O_5 and WO_3 from ZrO_2 , the latter remaining insoluble, while the WO_3 is quantitatively converted into soluble tungstate, and separated from tantalate and niobate by the sodium chloride method (§ 41).

CHAPTER X

THE SEPARATION OF THE EARTH ACIDS FROM TITANIA

Introduction

HAVING accomplished the separation of Group A—tantalic, niobic, and titanic oxides—from the elements of Group B, as described in Chapter IX, we are now faced with the central problem of earth-acid analysis, namely, the resolution of Group A into its constituents. This operation is conducted in two stages, viz., the separation of titania from the earth acids, discussed in the present chapter, and the separation of tantalum from niobium (Chapter XI).

The separation of titania from the earth acids, until recently an unsolved problem, can now be performed with reasonable accuracy as the result of our researches. The three separation methods evolved by us are based on differences in chemical behaviour which persist when the elements are in admixture :

(1) *The earth acids do not, whilst titania does, form a soluble salicylate complex.* Although the principle underlying the separation is not new, earlier attempts at using it involved the formation of refractory complex precipitates (Chapter II, 4). By first converting the three elements into their *soluble* oxalo-complexes, Schoeller and Jahn evolved the oxalate-salicylate method (XXI.), the most efficient of the three processes here described (§ 55).

(2) *The earth acids do not, whilst titania does, form a soluble sulphate, nitrate, or chloride.* The earliest attempts at a separation were based on the extraction of the bisulphate melt with water or dilute sulphuric acid, and were defeated by the strong tendency of the reacting elements to form complex colloidal suspensions and precipitates (Chapter II, 4). I have shown (XV.) that tannin counteracts this tendency ; hence, when the bisulphate melt is leached with acid tannin solution, titanium sulphate goes into solution, whilst the tannin complexes of the earth acids remain insoluble. This process, the pyrosulphate-tannin method (§ 54), is an indispensable adjunct of the oxalate-salicylate method.

(3) Tartaric hydrolysis forms the third separation method (Schoeller

and Deering (IX.)), already noticed in Chapter V (§25, 5). It consists in boiling a solution of the tartaric complexes with strong nitric or hydrochloric acid, which precipitates the earth acids, whilst titania is converted into soluble nitrate or chloride. This method was the first to be studied and, being the least accurate, has been superseded by the oxalate-salicylate method; however, it is a rapid process giving serviceable results on a centigramme scale (§ 53), the reaction being specific for the earth acids (Chapter XV).

Minute quantities of titania in the pentoxides are determined by colorimetry (§ 58).

§ 53. Separation by Tartaric Hydrolysis (Rapid Centigramme Process)

The mixed oxides (0.01 to 0.02 g.) are fused with 0.3 to 0.4 g. of bisulphate in a silica crucible; the product is dissolved by warming with about 5 ml. of 5 per cent. tartaric acid solution. The liquid is transferred to a small beaker, being freed if necessary from particles of grit, etc., by filtration through a small pad of filter pulp. The solution is boiled with 5 ml. of strong nitric acid in a total bulk of 25 to 30 ml. After five to fifteen minutes' heating, the beaker is allowed to stand a few hours; the precipitate is collected on a 5.5 cm. filter containing a little pulp, washed with dilute acid, ignited wet, and weighed.

The following results were obtained by Schoeller and Jahn (XIV.) by the above procedure:

Exp.	G. taken.		Precipitate Formed.	M_2O_3 Recovery.
	M_2O_3 .	TiO_2 .		
1	0.0009	—	After 15 minutes' boiling	0.0003
2	0.0030	—	„ 3-4 „ „	0.0030
3	0.0060	—	„ 2 „ „	0.0060
4	0.0090	—	„ 2 At once „	0.0090
5	0.0010	0.0050	After 15 minutes' boiling	0.0004
6	0.0035	0.0054	„ 4 „ „	0.0030
7	0.0060	0.0055	„ 2 „ „	0.0059
8	0.0090	0.0057	At once	0.0091

It will be seen that the results of Exps. 6 to 8, uncorrected for small amounts of co-precipitated titania, are serviceable. On a mg. scale

(Exps. 1 and 5) the results are low, and the pyrosulphate-tannin method (§ 54) is to be preferred. Still, the precipitate produced by tartaric hydrolysis is a certain proof of the identity of the earth acids.

The results obtained by Lundell and Knowles (IX.), working with 0.06 g. of pentoxide, have been given in § 25, 5. The method is not to be recommended for larger amounts (see tests, § 25, 5).

§ 54. Separation of Small Quantities of Earth Acid from Titania by the Pyrosulphate-tannin Method

This very simple procedure for tracing small quantities of earth acid in titania precipitates is an application of certain principles of colloid chemistry. It was deduced that when the bisulphate melt containing the oxides is in contact with a tannin dispersion, the small particles of the molecularly dispersed sulphates of potassium and titanium (and other soluble sulphates, *e.g.*, of zirconium) would be able to diffuse through the mesh-like structure of the liquid phase, whereas the larger aggregates of tantalum and niobic acid would be entangled and coagulated by the tannin sol as soon as they were formed during disintegration of the melt. The deductions were verified and confirmed experimentally.

Procedure. The mixed oxides (0.1 to 0.2 g.) are fused with 2 to 3 g. of bisulphate. The melt is made to solidify in a thin layer against the sides of the silica crucible. This is filled with hot reagent (1 g. tannin dissolved in 90 ml. of water and 10 of 1 : 1 sulphuric acid) and gently heated, the melt disintegrating into small detached fragments. The contents of the crucible are transferred to a 250-ml. beaker, and the crucible is rinsed with reagent (25 to 80 ml.) and discarded. The red liquid is heated to boiling, the particles of the melt being manipulated with a glass rod, and is left in the cold for some hours or overnight. The precipitate, P^1 , is collected, washed with 5 per cent. sulphuric acid, ignited, and weighed as $(Ta, Nb)_2O_5$.

If the proportion of titania in the mixed oxides is high, the ignited P^1 may be re-treated by the same method, yielding P^2 . The residual titania in P^1 or P^2 is determined colorimetrically (§ 58), M_2O_5 being obtained by difference. (Recovery of titania from the filtrate : § 55.)

The above method was originally proposed by Schoeller (XV.) for the separation of titania and zirconia from the earth acids, and tested by Schoeller and Jahn (XXI.) prior to its application in the standard procedure for the separation of titania from the earth acids (§ 55), with the following results :

Exp.	G. taken.		P^1	P^2	TiO_2 in P^1	M_2O_3 in P^1	M_2O_3 Error.
	M_2O_3	TiO_2					
1	0.0061	—	0.0060	—	—	0.0060	— 0.0001
2	0.0039	0.0100	0.0041	—	0.0004	0.0037	— 0.0002
3	0.0044	0.0200	0.0050	—	0.0008	0.0042	— 0.0002
4	0.0046	0.0420	0.0062	—	0.0019	0.0043	— 0.0003
5	0.0073	0.0606	0.0092	—	0.0022	0.0070	— 0.0003
					in P^1	in P^1	
6	0.0055	0.1012	0.0087	0.0052	0.0001	0.0051	— 0.0004
7	0.0078	0.1502	0.0149	0.0068	0.0003	0.0065	— 0.0013
8	0.0058	0.2034	0.0145	0.0053	0.0003	0.0050	— 0.0008

The figures show that the recovery is slightly incomplete, hence the negative error increases as the result of re-treatment.

§ 55. The Oxalate-salicylate Method

When an oxalate solution of the mixed oxides is treated with sodium salicylate, the characteristic orange colour of the salicylic titanium complex is produced. If now the oxalate ion is removed from the solution by addition of calcium chloride, a mixed precipitate of calcium oxalate and the salicylic complexes of tantalum and niobium (major fraction) is obtained, whilst the titanium complex remains in solution. The precipitation of the earth acids being incomplete, the titania fraction is recovered from the filtrate by precipitation with tannin and ammonium acetate, and the ignited precipitate is treated by the pyrosulphate-tannin method, which furnishes the minor earth-acid fraction. The major fraction is recovered from the oxalate precipitate by solution in hydrochloric acid, destruction of the oxalate with permanganate, and precipitation of the earth acids with tannin. Double treatment is necessary unless the amount of titania is very small (less than 0.01 g.).

Procedure. The weighed mixed oxides (about 0.25 g.) are brought into solution by fusion with potassium bisulphate (3.0 g.) in a silica crucible and treatment of the mass with a hot, strong solution of ammonium oxalate (2.0 g.) in an 800-ml. beaker. If any grit or insoluble matter remains, it should be collected on a small filter, washed with hot water, ignited, and the weight noted. Sodium salicylate B.P. (5 g.) dissolved in hot water is added to the boiling solution (bulk, 250 ml.), which is stirred and precipitated with a moderate excess of 20 per cent. calcium chloride solution, added gradually in small portions. The solution must not be allowed to cool; after a few minutes'

settling on the water-bath, the supernatant liquid is tested for complete precipitation with a little calcium chloride, and filtered at once by suction on an 11-cm. No. 40 Whatman filter supported by a platinum cone. The precipitate is washed with a hot 2 per cent. sodium salicylate solution until the washings are colourless. The yellow filtrate and washings (F^a) are transferred to another 800-ml. beaker and heated to boiling.

Major Earth-acid Fraction, P^1 . The oxalate precipitate is returned to the precipitation vessel, the filter being spread against the side of the beaker; the paper is washed with hot water, followed by 40 to 50 ml. of hydrochloric acid (1 : 1), and again with water, then ignited, and the ash added to the solution. This is heated and cautiously treated with excess of saturated permanganate solution (about 60 ml.). The froth formed during the manipulation may rise to the top of the beaker, and a wash-bottle with hot water is kept at hand to wash it down. When the deep-brown colour of the boiling-hot solution shows oxidation to be complete, a little tannin solution is added for the reduction of the manganic oxide. A fresh solution of 1 g. of tannin is added, and the solution is boiled for two minutes. The precipitate, P^1 , is left to settle, mixed with filter pulp, filtered off under gentle suction, washed with ammonium chloride solution, and ignited wet in a silica crucible.

Intermediate Fractions, p^1 , P^{1a} . (1) The filtrate from P^1 is neutralised with ammonia (1 : 1), slightly acidified with acetic acid, treated with 10 g. each of ammonium acetate and chloride, boiled down to 300 ml., and another 0.5 g. of tannin is added. After settling overnight, the small precipitate, p^1 , is collected and washed as P^1 .

(2) The boiling, yellow filtrate F^a (*supra*) is treated with 10 g. each of ammonium acetate and chloride, and a fresh solution of 1 to 2.5 g. of tannin (about twelve times the weight of the titania). The voluminous red precipitate, P^{1a} , is left to settle on the water-bath, and filtered off under gentle suction on a 12.5 cm. filter for quantities up to 0.15 g.; with larger amounts the precipitate is divided between two filters. After being washed in the same way as P^1 , the precipitate is ignited in a silica crucible, together with p^1 .

Minor Earth-acid Fraction, π^1 . The ignited precipitates ($p^1 + P^{1a}$) are fused with bisulphate (1 to 3 g.), and the cold fusion product is submitted to the pyrosulphate-tannin method (§ 54). The precipitate, π^1 , is collected, washed with 5 per cent. sulphuric acid, ignited, and added to P^1 . The filtrate from π^1 , containing the major titania fraction, is reserved.

Re-treatment of the Combined Earth-acid Fractions. The precipitates ($P^1 + \pi^1$) are once more subjected to the whole process so far described. The ammonium oxalate solution of the bisulphate melt is filtered if necessary, any residue being ignited and treated with hydrofluoric acid and a drop of sulphuric acid in a small platinum cup; the residue, if any, is fused with a speck of bisulphate, taken up with a few ml. of ammonium oxalate solution, and added to the bulk.

The re-treatment yields a *major earth-acid fraction*, P^2 , and small *intermediate fractions*, p^2 and P^{2a} ; these are combined and worked up by the pyrosulphate-tannin method for the *minor earth-acid fraction*, π^2 , the filtrate from which (*minor titania fraction*) is added to that from π^1 .

The final products of the separation are: ($P^2 + \pi^2$), which is weighed as $(Ta, Nb)_2O_5$; if bulky, its weight should be checked after lixiviation and another ignition prior to the separation of tantalum from niobium (Chapter XI); and the combined filtrate from π^1 and π^2 , containing the titania.

Determination of the Titania. This could be taken by difference, (the weight of ($P^2 + \pi^2$) being subtracted from that of the mixed oxides taken), but we recommend its direct determination in all accurate work as a check on the determination of the earth-acids, to which we will return in § 56. For the recovery of the titania there is a choice of two procedures.

(a) For smaller amounts, the combined filtrate from π^1 and π^2 is diluted, nearly neutralised with ammonia, and boiled with a large excess of ammonium acetate and chloride. The red precipitate is washed with ammonium chloride solution containing a little tannin, ignited, purified by leaching, ignited, and weighed; if not perfectly white, an allowance for ferric oxide may be necessary.

(b) For large amounts, the combined filtrate is evaporated with nitric and sulphuric acids for the destruction of the tannin. The titania in the filtered solution is determined by neutralisation with sodium carbonate and hydrolysis with sodium thiosulphate; the ignited precipitate should be leached before the final weighing.

§ 56. Calculation of Results

The test separations by Schoeller and Jahn (XXI.) must be studied for a computation of the errors incurred in the oxalate-salicylate method. Table I reproduces the data given in the original paper. The titania in the recovered pentoxides ($P^2 + \pi^2$) was determined colorimetrically (§ 58).

TABLE I

Exp.	G. taken.		Found TiO ₂	P ¹	P ¹ Leached.	π^1	P ¹ + π^1	M ₂ O ₅ Error.
	M ₂ O ₅	TiO ₂						
1	Ta ₂ O ₅ 0.2023	0.0516	0.0508	0.2036	0.1937	0.0078	0.2015	- 0.0008
2	Nb ₂ O ₅ 0.2027	0.0513	0.0512	0.2025	0.1954	0.0049	0.2003	- 0.0024
3	Nb ₂ O ₅ 0.1965	0.0535	0.0531	0.1963	0.1890	0.0053	0.1943	- 0.0022
4	Ta ₂ O ₅ 0.0335	0.2010	0.1986	0.0314	0.0266	0.0073	0.0339	+ 0.0004
5	Nb ₂ O ₅ 0.0439	0.2067	0.2068	0.0424	0.0368	0.0071	0.0439	0.0000
6	M ₂ O ₅ 0.1257	0.1176	0.1173	0.1273	0.1225	0.0033	0.1258	+ 0.0001

Titania. We will first consider the error incurred in the titania determination, by collating the quantities taken and recovered. In doing so, we have to omit Exp. 4, in which a manipulative accident was responsible for a loss of 0.0024 g. TiO₂.

TABLE II

Exp.	G. TiO ₂		TiO ₂ in (P ¹ + π^1)	Total Recovery.	Error.
	Taken.	Recovered.			
1	0.0516	0.0508	0.0008	0.0516	0.0000
2	0.0513	0.0512	0.0006	0.0518	+ 0.0005
3	0.0535	0.0531	0.0007	0.0538	+ 0.0003
5	0.2067	0.2068	0.0007	0.2075	+ 0.0008
6	0.1176	0.1173	0.0009	0.1182	+ 0.0006

The figures prove that (with the exception of Exp. 1) *the titania recovery error is positive if the small quantity of residual titania in (P¹ + π^1) is added to the titania result.* The excess is due to a fraction of a mg. of earth acid escaping flocculation in the pyrosulphate-tannin method. Within the limits of experimental error, this + error and the - error due to retention of titania by the pentoxides cancel each other, hence *the amount of titania recovered from the filtrates from π^1 and π^2 is to be taken as the nearest approximation to the true titania content.*

Earth Acid. In order to assess the earth-acid error we will now collate the total quantities taken and recovered.

The results disclose a negligible recovery error in Exps. 4 to 6 with lower M₂O₅ contents, the negative error in Exp. 4 being more than accounted for by the loss of 0.0024 g. due to the accident in the titania recovery (*supra*). Exps. 1 to 3—high earth-acid

UNSUCCESSFUL PROCESSES

TABLE III

Exp.	G. taken.			Recovered.			Total Recovery Error.
	M_2O_3	TiO_2	Sum.	$P^2 + \pi^2$	TiO_2	Sum.	
1	0.2023	0.0516	0.2539	0.2015	0.0508	0.2523	- 0.0016
2	0.2027	0.0513	0.2540	0.2003	0.0512	0.2515	- 0.0025
3	0.1965	0.0535	0.2500	0.1943	0.0531	0.2474	- 0.0026
4	0.0335	0.2010	0.2345	0.0339	0.1986	0.2325	- 0.0020
5	0.0439	0.2067	0.2506	0.0439	0.2068	0.2507	+ 0.0001
6	0.1257	0.1176	0.2433	0.1258	0.1173	0.2431	- 0.0002

contents—show a more substantial negative error, niobic being recovered less completely than tantalic oxide. Having accounted for a fraction of a mg. of pentoxides in the titania fraction obtained by the pyrosulphate-tannin method, we conclude that about 1 to 2 mg. of earth acid escapes recovery in the oxalate-salicylate method. Hence we adopt the rule that *the total recovery error is to be added to the pentoxide result, and subsequently apportioned between the two pentoxides after tannin separation* (§ 61).

§ 57. Unsuccessful Separation Processes

As a matter of theoretical interest, some of the difficulties met with in attempting the separation of titania from the earth acids may here be briefly described. Schoeller and Deering (IX.) investigated certain processes found in the literature, including three based on the formation of a soluble salicylic titanium complex.

(1) Muller's proposed method¹ consists in fusing the mixed oxides with potassium carbonate (5 g.), leaching the mass with water, and boiling the liquid with 15 g. of salicylic acid for three to four hours. The precipitate must be re-treated, several times if required, *i.e.*, as long as the salicylic acid solution becomes yellow on boiling. Our check tests proved each treatment to result in a substantial loss of pentoxide before the quantitative removal of the titania had been effected. The insoluble residue R^2 from the second treatment showed the following composition :

Exp.	G. taken.		R^2	TiO_2 in R^2	M_2O_3 in R^2	M_2O_3 Error.
	M_2O_3	TiO_2				
1	0.1007	0.1050	0.0958	0.0025	0.0933	- 0.0074
2	0.1500	0.0530	0.1359	0.0043	0.1316	- 0.0184
3	0.2004	0.0105	0.1914	0.0014	0.1900	- 0.0104

(2) According to directions found in Mellor's *Treatise on Quantitative Inorganic Analysis*,² the precipitate produced by hydrolysis of the

¹ *J. Amer. Chem. Soc.*, 1911, 33, 1506.

² London, 1913, p. 504.

solution of the bisulphate melt is "boiled for 3 or 4 hours with a large excess of salicylic acid. The titanic oxide dissolves, while the niobic and tantalum oxides remain insoluble." When working in accordance with these directions, we found that "metatitanic" acid produced by the hydrolysis of a titanic sulphate solution is insoluble in salicylic acid or ammonium salicylate solution. The hydrolysis precipitate from 0.0519 g. of pentoxides and 0.0522 g. titania was boiled for three hours in a bulk of 500 ml. with 15 g. of salicylic acid. The filtrate had a pale yellow tint, and the insoluble fraction weighed 0.1014 g., almost as much as the sum of the oxides taken.

(3) The precipitate produced by ammonia in hot or cold titanic sulphate solutions was found to be completely soluble in salicylic acid or ammonium salicylate solutions. In applying the process to mixed precipitates produced by ammonia in oxalate solutions, we failed to extract the whole of the titania even after three treatments:

	G. taken.		TiO ₂ extracted in one treatment.
	M ₂ O ₃	TiO ₂	
Nb ₂ O ₅	0.1023	0.1026	0.0802
"	0.1030	0.1010	0.0805
(Ta, Nb) ₂ O ₅	0.1008	0.0509	0.0419
"	0.2014	0.0408	0.0210
"	0.3004	0.0315	0.0148

This is another typical instance of unsuccessful extraction of a complex precipitate. Still less favourable results than the above were obtained by us in an attempt to apply alkaline mannitol solution, a reagent proposed by Hauser and co-workers.¹ For fuller details of our critical investigations the original paper (IX.) may be consulted.

§ 58. Colorimetric Determination of Titania

Weller's colorimetric method² is a valuable adjunct in earth-acid analysis, as it permits traces of titania to be determined in the pentoxides without recourse to a separation (Chapter II, 11). Although the bisulphate melt of the pentoxides is soluble in dilute sulphuric acid and hydrogen peroxide, the tint of the solution does not match that of the standard titanium solution. We always work in oxalate solution.

Procedure. The pentoxide to be tested (*e.g.*, 0.2 g.) is fused in a silica crucible with 3 g. of bisulphate. The melt is dissolved in 60 to 80 ml. of saturated ammonium oxalate solution, the liquid is transferred to a 200-ml. graduated flask, cooled, treated with 50 ml. of 10 per cent. sulphuric acid into which a little sodium

¹ Hauser, *Z. anorg. Chem.*, 1908, 60, 231; Hauser and Finkh, *Ber.*, 1909, 42, 2270; Hauser and Herzfeld, *Zentr. Min.*, 1910, 78.

² *Ber.*, 1882, 15, 2599.

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peroxide has been sprinkled, and the volume is adjusted. An aliquot portion is transferred to a Nessler tube. The standard is prepared from the same quantities of bisulphate, oxalate solution, and acid as those contained in the aliquot portion, and is titrated with a solution of known titania content (1 ml. = 0.0001 g. TiO_2) until the tints are even.

Alternatively a small portion of the oxide to be tested (0.01 to 0.02 g.) may be weighed up, dissolved as before with smaller quantities of reagents, and the whole of the solution tested. If it is desired to recover the oxide, the solution is transferred to a beaker, neutralised with ammonia, treated with ammonium chloride, and boiled with enough tannin to reduce the peroxide and precipitate the earth acid (0.3 to 0.5 g.). The precipitate is collected, washed with ammonium chloride solution, and ignited. It may be weighed as a check before being returned to the bulk. We use this procedure to check the purity of pentoxide precipitates prior to the separation of tantalum from niobium.

If the operator desires to know the approximate titania content of an earth-acid mineral before proceeding with its analysis, he may employ the direct colorimetric method, using 0.02 to 0.05 g. of mineral. This is fused with bisulphate, the melt is dissolved in ammonium oxalate solution, and the solution is tested with acidified hydrogen peroxide.

SPECIAL METHOD

§ 59. Rapid Approximate Separation of Titanium and Zirconium from Tantalum and Niobium

Prior to the discovery of the group separation by tannin (Chapter IX), we intended attacking the separation problem by the pyrosulphate-tannin method (§ 54). Whilst the latter is much simpler and more rapid, the former is undoubtedly more accurate. However, the pyrosulphate-tannin method can be used with advantage in cases where it is desired to obtain information as to the composition of an oxide mixture by a rapid method without regard to the highest degree of accuracy attainable. The method will find a place in technical alloy and ore analysis.

Procedure. The mixed oxides (0.1 g. for higher pentoxide, 0.2 g. for higher dioxide, contents) are fused with 2 to 3 g. of potassium bisulphate, and the melt is extracted with a 1 per cent. tannin solution in 5 per cent. sulphuric acid, as described in § 54. The insoluble tannin complexes of tantalum and niobium, *TP*, are collected, washed with 5 per cent. sulphuric acid, ignited, and weighed in a silica crucible. For their certain identification and

as a purity test, the weighed *TP* is again fused with bisulphate, the melt is dissolved in tartaric acid (§ 8), and the solution (filtered if necessary) is submitted to tartaric hydrolysis (§ 11). The precipitate is collected, washed with dilute hydrochloric acid, ignited, and weighed as $(Ta, Nb)_2O_5$.

The filtrate from *TP*, containing titanium and zirconium, is boiled down with 10 ml. of strong sulphuric acid until it darkens and foams. It is then treated with small portions of strong nitric acid till clear and colourless, and heated more strongly until copious white fumes are given off. After cooling, 100 ml. of cold water are added, and the cooled solution is treated with excess of hydrogen peroxide. The zirconium is precipitated with a large excess of ammonium phosphate; the precipitate is mixed with pulp, collected under suction, washed with ammonium nitrate solution, ignited, and weighed as ZrP_2O_7 .¹ The approximate factor 0.46 for the conversion into ZrO_2 may be used. The titania in the filtrate, if subordinate, is determined colorimetrically; if large, it may be taken by difference.

The following results of thirteen test analyses by Schoeller (XV.) give an idea of the degree of accuracy of which the method is capable. The tests were run as rapid exploratory determinations, no attempt being made at introducing analytical refinements. All the pentoxide precipitates (*TP*) were weighed. Titania and zirconia, when subordinate, were determined as described above; when present in large amounts, they were taken by difference. Quantities computed by difference are shown in italics in the table below.

The composition of the "unknown" mixtures was varied in such a manner as to present the greatest diversity, from the total absence of each constituent to its forming the bulk of the mixture. Let *M* and *m*

Type.	G. M_2O_5		G. TiO_2		G. ZrO_2	
	Taken.	Found.	Taken.	Found.	Taken.	Found.
<i>mT</i>	0.0058	0.0077	0.0922	0.0903	<i>nil</i>	<i>nil</i>
<i>Tz</i>	<i>nil</i>	<i>nil</i>	0.0964	0.0937	0.0058	0.0067
<i>mZ</i>	0.0072	0.0070	<i>nil</i>	<i>nil</i>	0.1054	0.1056
<i>iZ</i>	<i>nil</i>	<i>nil</i>	0.0052	0.0056	0.0965	0.0961
<i>Mt</i>	0.0900	0.0900	0.0033	0.0055	<i>nil</i>	<i>nil</i>
<i>Mz</i>	0.0925	0.0894	<i>nil</i>	<i>nil</i>	0.0050	0.0060
<i>mTz</i>	0.0050	0.0046	0.0950	0.0946	0.0092	0.0100
<i>mtZ</i>	0.0054	0.0042	0.0056	0.0055	0.0936	0.0944
<i>MtZ</i>	0.0908	0.0900	0.0030	0.0020	0.0044	0.0043
<i>mTZ</i>	0.0054	0.0046	0.0799	0.0686	0.0708	0.0739
<i>MTz</i>	0.0723	0.0757	0.0716	0.0673	0.0050	0.0059
<i>MtZ</i>	0.0704	0.0720	0.0054	0.0044	0.0736	0.0730
<i>MTZ</i>	0.0620	0.0625	0.0643	0.0603	0.0628	0.0663

¹ Hillebrand and Lundell, *op. cit.*, p. 446.

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represent large and small amounts of $(Ta, Nb)_2O_5$ respectively; T and t , large and small amounts of TiO_2 ; Z and z , large and small amounts of ZrO_2 ; these values were permuted as shown in column 1, under "Type." The cases MT , MZ and TZ were disregarded as superfluous. The pentoxide preparation used contained 61.4 per cent. of Ta_2O_5 , and 38.6 per cent. of Nb_2O_5 .

In the same paper I have criticised the salicylic-acid method of Noyes and Bray¹ for the separation of Ti from Zr, Ta, and Nb, which consists in boiling the mixed hydroxides with 5 g. of sodium carbonate and 15 g. of salicylic acid in a total bulk of 400 ml. for two hours. Noyes and Bray claim that the whole of the titania passes into solution, whilst the other hydroxides remain undissolved. In my check tests with the method (XV.), the extraction of the titania was almost uniformly poor and much lower still than in the similar experiments by Schoeller and Deering (IX.) reproduced in § 57, 3. Here again we have a case of unsuccessful extraction of a complex precipitate.

A re-investigation of Dittrich and Freund's salicylic-acid method² for the separation of titanium from zirconium was conducted by Powell and Schoeller (XVIII.), who found that it was not strictly quantitative.

¹ *A System of Qualitative Analysis for the Rare Elements*, New York, 1927. Procedure 41, p. 98.

² *Z. anorg. Chem.*, 1908, 56, 344.

CHAPTER XI

THE SEPARATION OF TANTALUM FROM NIOBIUM

Introduction

THE second and final step in the analysis of Group A is the determination of tantalum and niobium in the mixed pentoxides. The classic separation method of Marignac, whilst assured of enduring fame as having settled the separate identity of tantalum and niobium, received an almost fatal blow as an analytical process by our discovery of the tannin method. Marignac himself was aware of the inherent defect of the fluoride method, namely, its failure to deal with small quantities of tantalum, due to the relative solubility of potassium fluorotantalate. For this if for no other reason, his process must yield to the tannin method, which is the only wet method capable of detecting and determining the smallest quantities of tantalum in presence of large amounts of niobium (§ 63).

The tannin method (explained in § 61) has likewise superseded the unreliable oxidimetric processes for niobium, proposed as an alternative to the gravimetric separation of the two elements (§ 60). The determination of traces of niobium in presence of much tantalum is discussed in § 64.

§ 60. Inaccuracies of the Oxidimetric Method

Repeated attempts have been made at circumventing the actual separation of tantalum from niobium by a volumetric determination of niobium in the mixed oxides. The published processes rely on the reduction of niobium pentoxide to a lower oxide, and re-oxidation of the latter by means of permanganate. It is not intended here to give working directions for any of these processes, for I hold them to be faulty in execution and therefore of no further use since the introduction of the tannin method. Soluble niobium compounds can be reduced to the sesquioxide stage, but the reduction is never stoichiometric. The supposition that intermediate oxides such as Nb_3O_5 , Nb_8O_{13} , $Nb_{10}O_{17}$, etc., are formed may be dismissed as unlikely; Treadwell¹ gave a satisfactory explanation for the erratic behaviour of niobium on reduction when he inferred that the dissolved compound undergoes partial hydrolysis with formation of a colloidal phase, only the portion in true molecular solution being reduced to the sesquioxide.

A critical investigation was undertaken by Schoeller and Waterhouse (III.), who tested the methods of Metzger and Taylor² (solution

¹ *Helv. Chim. Acta*, 1922, 5, 806.

² *J. Soc. Chem. Ind.*, 1909, 28, 818.

of the bisulphate melt in sulphuric and succinic acids and reduction by amalgamated zinc in a Jones' reductor) and of Levy¹ (reduction of the fluoride solution with granulated zinc), and elaborated a process suggested by Giles² (solution of potassium carbonate melt in phosphoric acid and reduction by zinc dust). The experimental evidence proved these processes to be unreliable; the empirical factors obtained by Metzger and Taylor and by Levy could not be duplicated, and every time a slight variation in the working conditions occurred, a serious deviation in the factor ensued. Similar observations were made by Treadwell. The following compilation of factors illustrates the unreliability of the oxidimetric method:

(a) <i>Metzger and Taylor's method.</i>		G. Nb ₂ O ₅ per ml. (o'1 N).
Metzger and Taylor's factor	.	0.007052
Wells's factor (<i>Amer. J. Sci.</i> , 1911, 31, 439)	.	0.007767
Schoeller and Waterhouse (III.), 4 tests	.	0.007424
2 tests (purer Zn).	.	0.008139
Wells's later factor (<i>J. Amer. Chem. Soc.</i> , 1928, 50, 1020)	.	0.00755
(b) <i>Levy's method.</i>		
Levy's factor	.	0.00833
Schoeller and Waterhouse, 9 tests	.	0.01006
(c) <i>Giles's proposed method.</i>		
Schoeller and Waterhouse, 11 tests	.	0.006990
6 tests (more Zn)	.	0.007261
(d) Stoichiometric factor (Nb ₂ O ₅ + 2O = Nb ₂ O ₃)	.	0.006655

We concluded that methods furnishing an empirical factor are unreliable, and that the criterion of accuracy should be a stoichiometric factor, indicating reduction to a definite oxide. The late Dr. W. F. Hillebrand, in a letter to me dated October 21st, 1924, expressed himself as follows: "I agree entirely with the conclusions reached by you and Mr. Waterhouse on the volumetric estimation of columbium." More recently, Tschernichow and Karssajewskaja,³ as a result of a careful re-investigation of the subject, confirmed our conclusions as to the unreliability of the method, due to the uncertain degree of reduction of niobic oxide.

§ 61. Separation by the Tannin Method

The separation is based on the differential stability of oxo-tantalalic and oxo-niobic acids in presence of tannin in slightly acid solution, a reaction discovered by Powell and Schoeller in 1920 (IV.). The principle is the same as that underlying our method for the separation of Group A from Group B (Chapter IX), in which tantalum, niobium, and titanium are quantitatively precipitated from almost neutral oxalate solution in presence of ammonium chloride, whilst the more basic oxides remain in solution. In the case of a solution containing only tantalum and

¹ *Analyst*, 1915, 40, 204.

² *Chem. News*, 1909, 99, 1.

³ *Z. anal. Chem.*, 1934, 99, 398.

niobium, it is possible to effect a separation by carefully regulated addition of tannin and ammonia, tantalum being precipitated more readily from slightly acid solution. The tantalum complex is yellow, the niobium complex red; co-precipitation of niobium with the tantalum is indicated by the orange colour of the tannin precipitate. Fractional precipitation is unavoidable, because the tantalum cannot be quantitatively precipitated without contamination with niobium if the tantalum concentration is much lower than the niobium concentration.

The standardised procedure, described by Schoeller (XXIV.), furnishes three fractions, namely, (1) a niobium-free tantalum fraction (yellow precipitates); (2) a mixed or intermediate fraction (orange to red precipitates); and (3) a niobium filtrate free from tantalum. (With low Ta : Nb ratios, a yellow precipitate will not be obtained in the first fractionation.)

Quantitative separation is achieved by systematic re-treatment of the mixed or intermediate fraction; this is fractionated as before, yielding another three fractions, the intermediate one of which is fractionated in its turn (and so on, if necessary). All the yellow, pure tantalum precipitates are ignited together; the pure niobium filtrates are combined.

After one or two fractionations the intermediate fraction will have been reduced to something of the order of 0.02, or even less than 0.01 g. If the operations are properly performed, the total error will be confined to that incurred in the final treatment of the last intermediate fraction. At that stage it is necessary, in order to counteract incomplete recovery of the tantalum, to produce a slightly niobiferous final tantalum fraction (*i.e.*, pale orange precipitate). This conforms with the principle I have previously applied in the determination of platinum: "If a substance cannot be precipitated quantitatively in one operation without undue contamination, it may be feasible to obtain it in two fractions. The first or major fraction should be pure. The minor fraction completes the precipitation; it is not pure, but, if sufficiently small, it renders the error negligible for practical purposes."¹

Reagents. Potassium bisulphate, silica-free. Ammonium oxalate, saturated solution. Ammonium chloride, saturated solution. Tannin, freshly-prepared 2 per cent. solution. *N* ammonia. Wash-liquor for tannin precipitates: 2 per cent. ammonium chloride. All reagents should be free from calcium.

Apparatus. Tared silica crucible *s* for bisulphate fusion. A pair of fractionation beakers (600 ml.; smaller size for end-

¹ *Analyst*, 1930, 55, 550.

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fraction). Tared porcelain crucible, *p*, for tantalum precipitates. Squat beaker *B* (800 ml.), for niobium filtrates. Apparatus for suction filtration (platinum or hardened paper cone). Whatman filters No. 40, 12.5 ml. and smaller. For the smaller precipitates, simple filtration through Whatman No. 41 paper. Filter pulp. Burette for tannin.

Notation. The precipitates obtained in the first fractionation are designated, in succession, P^1 , P^{1a} , P^{1b} , P^{1c} ; those obtained in the second fractionation (*i.e.*, re-treatment of the first intermediate), as P^2 , P^{2a} , P^{2b} ; those from the third fractionation (re-treatment of the second intermediate) as P^3 , P^{3a} , P^{3b} , etc.

Procedure. The mixed pentoxides (0.2 to 0.3 g., or more if poor in tantalum) are fused with potassium bisulphate in the crucible *s*, and the product is dissolved in hot ammonium oxalate solution (75 to 100 ml.). Any small residue is filtered off and re-treated, and the resulting solution (filtered if necessary) is added to the main portion.

First Fractionation. The boiling solution (250 ml.) is cautiously titrated with tannin reagent; if this produces a yellow coloration, enough tantalum is present to yield a yellow (niobium-free) P^1 , provided the addition of tannin is interrupted before the yellow tint deepens to orange; see (*a*). If, however, an orange or red coloration is produced, P^1 will contain niobium as well as tantalum; see (*b*).

(*a*) *The Coloration is Yellow.* Four precipitates are produced in the first fractionation (or three if P^{1a} is orange instead of yellow):

Tantalum fraction: P^1 (main fraction), P^{1a} .

Intermediate (mixed) fraction: P^{1b} , P^{1c} .

The four precipitations are done in one day, filtration of P^{1c} taking place the next morning.

P^1 (*yellow*): the gradual addition of tannin is continued while the boiling liquid is being stirred; with high tantalum contents a yellow precipitate will be formed. Any orange coloration appearing at the point of incidence of the reagent is made to disappear by agitation. The addition of tannin is interrupted before any permanent colour-change takes place; in no case is more than 50 ml. of tannin reagent added. Complete flocculation is brought about by addition of 30 to 50 ml. of saturated ammonium chloride solution; partial neutralisation with *N* ammonia to induce precipitation is hardly ever necessary in the case of P^1 . The solution is boiled gently for five to ten minutes, and left on the water-bath for half an hour. The precipitate P^1 is collected,

well washed (return to precipitation beaker), and ignited in crucible *p*.

P^{1a} (yellow): the filtrate from *P¹* is boiled down while the precipitate is being washed; the total volume of filtrate and washings is kept approximately constant during each fractionation. The boiling solution is cautiously treated with *N* ammonia until a permanent cloudiness appears, then slowly titrated with tannin, being agitated meanwhile. The bulky *P¹* having been eliminated, it is usually possible, by observation of the delicate colour changes, to obtain an additional yellow fraction *P^{1a}*. This is treated, as before, by boiling and digestion on the water-bath. If yellow, the washed *P^{1a}* is added to *P¹*. If, however, *P^{1a}* appears orange after settling on the water-bath, the gradual addition of *N* ammonia and tannin should be continued; this will produce a larger precipitate of decided orange colour, *i.e.*, the first intermediate precipitate *P^{1b}*.

P^{1b} (orange): the concentrated filtrate from the yellow precipitate *P^{1a}* is boiled, stirred, treated with *N* ammonia until slightly cloudy, and titrated with tannin until a deep orange precipitate is produced. The ignited *P^{1b}* should amount to 0.01 to 0.02 g. After boiling, digestion on the water-bath, and filtration, the washed precipitate is ignited in crucible *s*.

P^{1c} (red): the concentrated filtrate from *P^{1b}* is treated exactly as the preceding filtrate, but the red precipitate *P^{1c}*, after digestion on the water-bath, is set aside overnight before filtration. The washed *P^{1c}* is added to *P^{1b}*; the tantalum-free filtrate *F^{1c}* is concentrated in beaker *B*.

The precipitation of the intermediate fraction in two portions is always advisable, as total precipitation of the tantalum has not necessarily taken place when incipient precipitation of niobium becomes evident: at low tantalum and high niobium concentrations the two stages overlap. If *P^{1b}* is orange at first and reddens with continued addition of ammonia and tannin, whilst *P^{1c}* is decidedly reddish at the time of its formation, it may safely be inferred that total precipitation of tantalum has been achieved.

Each fraction is weighed to the nearest mg.; the colour and weight of the precipitates are recorded as important guides, together with the amount of tannin added.

(*b*) *The Coloration is Orange to Red*. No tantalum fraction will be obtained. The mixed fraction, containing all the tantalum and some niobium, is produced in two portions, *P¹* and *P^{1a}*, which correspond with *P^{1b}* and *P^{1c}* of the preceding case.

P¹ (orange to red): the addition of tannin to the boiling solution is regulated from a minimum of 10 ml. (for low Ta : Nb ratios)

to about 20 ml. The precipitate is flocculated by addition of 30 ml. of the ammonium chloride solution,* if necessary a little *N* ammonia, boiling, and digestion on the water-bath. It is collected, washed, and ignited in crucible *s*.

P^{1a} (red): the concentrated, boiling filtrate from *P¹* is treated with a little *N* ammonia, followed by tannin; a red precipitate should be obtained, yielding about 0.02 g. of ignited oxide. The liquid is set aside overnight; *P^{1a}* is collected, washed, and added to *P¹*. The tantalum-free filtrate, *F^{1a}*, is concentrated in beaker *B*.

Second Fractionation. The weighed intermediate fraction (*P^{1b} + P^{1c}*) (case *a*), or the mixed fraction (*P¹ + P^{1a}*) (case *b*), is fused with bisulphate, and the product dissolved in ammonium oxalate solution.

The second fractionation is exactly like the first. The operations take place on a reduced scale; the manipulative details remain identical. The boiling oxalate solution is cautiously titrated with tannin, which produces either a yellow (*c*) or, if the tantalum content is very low, an orange to red (*d*), coloration.

(*c*) *Yellow Coloration.* Properly performed, the first fractionation of a tantalum-rich mixture gives a small intermediate fraction (*P^{1b} + P^{1c}*), the niobium-content of which is sufficiently low (see example *A* below) to enable the operator to complete the separation at this stage. The directions will be found under "*Final fractionation.*"

If, on the other hand, the original oxide mixture contained substantial quantities of both oxides, then the intermediate fraction will be heavier, and its re-treatment will constitute the penultimate fractionation. Three precipitations are carried out (four are hardly necessary):

P²: yellow. Ta fraction; to crucible *p*.

P^{2a}: yellow or orange (see below).

P^{2b}: orange to red. Mixed fraction; to crucible *s*.

The precipitate *P^{2a}* is disposed of according to its colour: if yellow, it is added to *P²*; if orange, to *P^{2b}*. It is not at all uncommon to obtain a yellow *P^{2a}*. The tantalum-free filtrate *F^{2b}* is added to beaker *B*.

(*d*) *Orange to Red Coloration* (very low tantalum content). Another mixed fraction, in two portions, will have to be produced, exactly as in the first fractionation (case *b*):

P²: orange to red. To crucible *s*.

P^{2a}: red. Collected next day; to crucible *s*.

The tantalum-free filtrate *F^{2a}* is added to beaker *B*. In the present case, (*P² + P^{2a}*) should not be subjected to final fractiona-

tion without an intervening third fractionation, which must yield a yellow head-fraction P^3 .

Final Fractionation. As explained above, the final tantalum fraction to be produced should be slightly niobiferous; hence the mixed fraction submitted to final fractionation should be as small as possible, and comparatively low in niobium. When to undertake the final fractionation is a matter for the operator's judgment, which must be based on each occasion on the colour as much as on the weight of the intermediate fraction to be treated. The examples given below are perhaps the best practical guide for this part of the process.

The intermediate fraction having been dissolved as before, the boiling solution (50 to 100 ml.) is treated with tannin until a pale orange coloration is obtained. Flocculation is induced by 10 to 20 ml. of ammonium chloride solution and a few drops of *N. ammonia*. Should the coloration be yellow, the final fraction can be obtained in two portions, a yellow precipitate first, and a pale orange one in the filtrate therefrom.

Determination of the Tantalum. The weight of the tantalum fraction must be corrected for adsorbed salts, silica (filter ash), and titania (see below). The combined ignited precipitates are leached with 2 per cent. hydrochloric acid, collected, strongly ignited, and weighed. The oxide is then fused with bisulphate, the product is dissolved in ammonium oxalate solution, and the slight residue is collected, well washed, ignited, and weighed as silica. The oxalate filtrate is treated according to § 58 for the colorimetric determination of the titania.

The result is calculated as follows: if the analysis has not involved a previous removal of titania by the oxalate-salicylate method, the sum of silica and any titania found by colorimetry, subtracted from the weight of the leached precipitate, gives the net weight of the tantalum oxide.

If, on the other hand, the pentoxides have been separated from titania by the oxalate-salicylate method, no allowance for titania is made; the weight of the silica is subtracted from that of the leached precipitate, and to this value is added a part of the recovery loss incurred in the oxalate-salicylate process (see § 56) in proportion to the tantalum-oxide content of the pentoxide fraction.

Determination of the Niobium. This oxide may be taken by difference, the balance of the recovery loss in the oxalate-salicylate method being added to the result if that process was used. For subordinate amounts of niobium we recommend a check determination: the combined niobium filtrates are boiled with 0.5 to 1 g. of tannin and a small excess of ammonia. The ignited (frequently

ferruginous) precipitate is fused with bisulphate, the mass is dissolved in ammonium oxalate, and any silica filtered off; the filtrate is neutralised with *N* ammonia and diluted with an equal volume of saturated ammonium chloride solution; the niobium is precipitated with tannin, as directed in § 49. The ignited precipitate is leached, ignited, weighed, and tested for titania like the tantalum precipitate.

Two test analyses by Schoeller (XXIV.) are reproduced below:

Example A. Taken: 0.2023 g. of Ta_2O_5 , 0.0550 g. of Nb_2O_5 .

Tannin solution ml.	Fractionations		Gross weight of precipitates	
	First	Second	Mixed fractions g.	Ta_2O_5 fractions g.
50	P^1 , yellow	- - - - -	- - - - -	0.1866
20	P^{1a} , yellow	- - - - -	- - - - -	0.0144
5	P^{1b} , orange	re-treated:	0.0070	
5	P^{1c} , red		0.0040	
18		P^2 , yellow	- - - - -	0.0042
		P^{2a} , pale orange	- - - - -	0.0008
		Gross weight of Ta_2O_5 fraction		0.0050
		Less leaching loss 0.0030 g., SiO_2 0.0012 g.		0.0042
		Net Ta_2O_5 found		0.2018

Mixtures rich in Ta_2O_5 provide the simplest case for separation. More than 90 per cent. of the Ta_2O_5 is recoverable as P^1 .

Example B. Taken: 0.0516 g. of Ta_2O_5 , 0.2006 g. of Nb_2O_5 , 0.0012 g. of TiO_2 .

Tannin solution ml.	Fractionations			Gross weight of precipitates	
	First	Second	Third	Mixed fractions g.	Ta_2O_5 fractions g.
20	P^1 , orange	re-treated:	- - - - -	0.0624	
5	P^{1a} , red		- - - - -	0.0160	
10		P^2 , yellow	- - - - -	- - - - -	0.0422
3		P^{2a} (see below)	re-treated:	0.0140	
1		P^{2b} reddish		0.0144	
5			P^3 , yellow	- - - - -	0.0114
			P^{3a} , pale orange	- - - - -	0.0034
			Gross weight of Ta_2O_5 fraction		0.0570
			Less leaching loss 0.0016 g., SiO_2 0.0027 g., TiO_2 0.0009 g.		0.0052
			Net Ta_2O_5 found		0.0518

In Example B the Ta_2O_5 : TiO_2 ratio was 43 : 1, or, in other words, the titania amounted to about 2 per cent. of the tantalum oxide (*cf.* § 62). The colour of P^{2a} (due to admixture of titania) was rather deceptive: the precipitate was intended to be added to P^2 , but, when packed on the filter (which is always the safest way to judge of the colour of the precipitates), it appeared too impure for a tantalum fraction; hence it was re-treated. Otherwise the separation was satisfactory.

The original separation method by Powell and Schoeller (IV.) need not here be considered, as it has been replaced by the standardised procedure described in this paragraph. The older paper gives the results of twenty-five test separations, with six check tests carried out by Dr. G. E. F. Lundell and Mr. H. B. Knowles in the U.S. Bureau of Standards. At the time of the publication of Section IV., the purification technique for tannin precipitates had not been perfected.

§ 62. Interference of Titanium (Tungsten)

The interference of titanium in the tannin separation of tantalum from niobium was quantitatively investigated by Schoeller and Powell (XI.), who observed that, at an acid concentration preventing co-precipitation of niobium with the tantalum, titanium was always co-precipitated to a certain extent; and that the admixture, unless minute, discoloured the otherwise yellow tantalum precipitate sufficiently to deprive the tannin method of its vital feature, viz., control of the separation by observation of the colour changes.

The interference of titanium in the tannin separation of tantalum from niobium was elucidated by Schoeller and Webb (XXXII.) during an investigation of the action of tannin on vanadium solutions, which will be discussed in § 75. We established a serial order of precipitability within Group A, titanium being placed between tantalum and niobium: Ta—Ti—Nb. From this it follows that, whilst tantalum can be separated from niobium by fractional precipitation, the interval of precipitation between two neighbouring elements in the series is too small to admit of a separation.

The discoloration of the tantalum-tannin complex caused by an admixture of titanium is in the direction of buff or brownish-yellow. The statement found in many text-books that tantalum gives a "light-brown" tannin precipitate must be based on observations made on impure tantalum preparations containing titanium.

The experiments of Schoeller and Powell (XI.) reproduced below should be studied with reference to the $Ta_2O_5 : TiO_2$ ratios and the colour of the precipitates:

Exp.	1	2	3	4	5	6
G. taken. { Ta_2O_5	0.1002	0.2016	0.0211	0.0520	0.0024	0.1686
{ Nb_2O_5	0.1017	0.0222	0.2004	0.1811	0.2154	0.0365
{ TiO_2	0.0056	0.0023	0.0022	0.0063	0.0094	0.0051
$Ta_2O_5 : TiO_2$	18	88	9.6	8.2	0.25	33
P^1	0.0834 (d)	0.1596 (a)	0.0191 (e)	0.0563 (c)	0.0100 (f)	0.1571 (g)
ΣP^1	0.1058 (d)	0.2043 (a)	0.0337 (d)	0.0651	0.0166 (f)	0.1721
ΣP^2	—	—	0.0263 (d)	0.0465 (d)	—	0.1400 (b)
P^3	(h)	—	—	(h)	0.0047 (e)	(h)
TiO_2 in last P	0.0039	0.0017	0.0015	0.0032	0.0013	0.0030

Colour of P: (a) yellow; (b) bright yellow; (c) pale orange; (d) orange; (e) reddish; (f) red; (g) pale buff.

(h) Fractionation not completed.

The above tests demonstrate the impossibility of separating tantalum from niobium by tannin in presence of more than a very subordinate amount of titanium. Exp. 2 proceeded normally.

The following is a safe rule : *If the $Ta_2O_5 : TiO_2$ ratio is lower than 50, the titania should first be eliminated by the oxalate-salicylate method. If the absolute amount of titania is below 0.01 g., double oxalate-salicylate treatment is unnecessary.* The titania content may be determined by a colorimetric pilot test on 0.01 to 0.02 g. of mixed oxides, which may be subsequently recovered (§ 58).

The following tests by Schoeller and Jahn (XXI.) on oxide mixtures with subordinate titania content show the amount of titania removed by a single application of the oxalate-salicylate method (notation of precipitates as in § 55) :

Exp.	G. taken		P^1	P^{1a}	π^1	TiO_2 in ($P^1 + \pi^1$)	
	M_2O_5	TiO_2					
1	Nb_2O_5	0.1814	0.0241	0.1805	0.0248	0.0021	0.0026
2		0.1814	0.0234	0.1801	0.0234	0.0030	0.0037
3		0.2027	0.0246	0.1971	0.0274	0.0038	0.0021
4	Ta_2O_5	0.1491	0.0249	0.1476	0.0247	0.0028	0.0019
5		0.1554	0.0122	0.1536	0.0120	0.0015	0.0007
6		0.1758	0.0254	0.1779	0.0212	0.0027	0.0049

Experiment 5, with the lowest titania content, shows a satisfactory elimination of the titania.

My advice to operators not too familiar with the tannin separation of tantalum from niobium is, to err on the side of caution. In cases of doubt, the titania should be eliminated first : the removal even of a few mg. strikingly improves the colour indications in the fractionation. The lower the tantalum content, the more imperative is the need for reducing the titania to a minimum.

Tungsten. A subordinate amount of tungsten, besides contaminating the earth-acid fractions, renders the fractionation less readily observed by reason of the slight brownish tinge of the tantalum precipitates ; this may not appear at once, but after a few minutes. The interference of tungsten is less pronounced than that of titanium. It is more evident with low Ta : W ratios ; the filtrates may show a brownish tinge. The two experiments here given were conducted by Schoeller and Jahn (XXVI.).

Exp.	G. taken		M_2O_5 Precipitate.	WO ₃ in Precipitate.
	M_2O_5	WO ₃		
1	{ Ta ₂ O ₅ 0·1546	0·0152	Ta fraction 0·1538	0·0018
	{ Nb ₂ O ₅ 0·1547		Nb „ 0·1625	0·0065
2	{ Ta ₂ O ₅ 0·0528	0·0150	Ta fraction 0·0582	0·0038
	{ Nb ₂ O ₅ 0·2023		Nb „ lost	—

Zirconium, being a member of tannin Group B (*i.e.*, less readily precipitated by tannin from oxalate solution than niobium), does not interfere with the determination of tantalum by fractional precipitation.

SPECIAL METHODS

§ 63. Determination of Small Amounts of Tantalum in Niobic Oxide

The tannin separation described in § 61 is the only method by which this determination can be accomplished; repeated fractionation is necessary. Powell and Schoeller's procedure (V.) is as follows.

Procedure. Several 1-g. portions are fused with 5-g. portions of bisulphate in silica crucibles. Each fusion is dissolved in 100 ml. of saturated ammonium oxalate solution, diluted to 400 ml., and boiled with 0·2 g. of tannin and 5 g. of ammonium chloride; neutralisation is unnecessary unless the precipitate does not flocculate. After standing overnight the precipitates are collected, washed with ammonium chloride solution, ignited, combined, and weighed. This concentrate, P^1 (in two portions if over 1 g.) is again submitted to the same process, yielding P^2 ; the latter is once more fused with a smaller quantity of bisulphate, etc., and if the head-fraction P^3 is yellow, a further precipitate, P^{3a} , should be produced. The concluding stages of the fractionation are the same as in § 61. In the last fractionation, the oxalate solution should be filtered prior to tannin precipitation to eliminate silica, calcium oxalate, etc., accumulated from the reagents used in the process.

It would be a mistake to work on portions of more than 1 g. of niobic oxide and add less than 0·2 g. of tannin for the production of P^1 in an endeavour to expedite the work. We have proved that if a deficiency of tannin is added to a solution of high niobium concentration, the precipitation of the tantalum may be incomplete as the large excess of niobic acid adsorbs the tannin required for the formation of the tantalum complex.

In dealing with an unknown sample of niobic oxide, the

operator should first satisfy himself as to its titania content (§ 58), and remove it, if necessary, after two or more fractionations, *i.e.*, when the weight of the tannin precipitate has been reduced to a little less than 0.2 g.

The following results were obtained in the analysis of three samples of niobic oxide (A to C).

Exp.		G. taken.	P^1	ΣP^2	ΣP^3	ΣP^4	Per cent. Ta ₂ O ₅	
A. (V.)	{	1	1.0012	0.225	0.0142	0.0034	0.0014	0.140
		2	0.5010	0.092	0.014	0.0030	0.0008	0.160
		{	1.0000	0.086	0.0145	0.0104	0.0047	0.157
			1.0000	0.0567				
			1.0000	0.0843				
B (V.)	{	4	1.0000	0.0296	0.0020	not weighed	0.0003	0.030
		5	1.0000	0.052	0.0030		0.0020	0.0005
C. (XXIV.)	6	{	1.0000	0.565	0.122	0.0360	0.0074 ¹	0.370
		1.0000						

Mr. A. R. Powell, having analysed sample C independently and in ignorance of my result, reported 0.32 per cent. of Ta_2O_5 in the material.

§ 64. Determination of Small Amounts of Niobium in Tantallic Oxide

(a) If the proportion of niobic oxide is not too small (*e.g.*, of the order of 0.5 per cent.), this determination can be effected by the tannin method, four 0.25-g. portions being treated separately. A pilot test for titania should be made first. Each portion is fused with 3 to 4 g. of bisulphate, and the boiling oxalate solution of the melt (250 ml.) is precipitated with 1 g. of tannin and 5 g. of ammonium chloride. The precipitate is filtered under suction, returned to the beaker, stirred up with ammonium chloride wash-liquor, again collected, washed, and discarded. The filtrate is precipitated with more tannin and a slight excess of ammonia, and the precipitate is collected as before and ignited. The combined precipitates from the four portions (the total weight of which should be less than 0.2 g.) are fused with 3 g. of bisulphate, and the oxalate solution of the melt is either subjected to the oxalate-salicylate method if the pilot test disclosed interfering amounts of titania, or again precipitated with tannin as before. The yellow precipitate is rejected, and the filtrate is worked up for the recovery of the remaining oxides; at this and the later

¹ This is ΣP^5 .

stages of the fractionation it is advisable to effect this by treating the boiling solution with tannin and 5 g. of pure ammonium acetate, and observe the colour of the precipitate before adding ammonia in slight excess. The niobium complex precipitated by addition of acetate has a fine red colour, whereas excess of ammonia leads to discoloration of the precipitate. The concluding stages of the fractionation are the same as those of the standard procedure (§ 61).

(b) If the niobic oxide content is less than 0.1 per cent., more than 1 g. of tantallic oxide should be taken, which renders the manipulation of the bulky precipitates inconvenient. In such cases recourse may be had to Marignac's reaction for a preliminary concentration of the niobium. Several g. of powdered tantallic oxide are dissolved by heating with excess of hydrofluoric acid in a platinum dish. Metallic tantalum is dissolved in warm hydrofluoric acid with dropwise addition of nitric acid. If any difficulty is experienced in dissolving the last of the oxide, the solution is filtered through a rubber funnel into a platinum or bakelite dish, the residue washed with water, ignited in a platinum crucible, and fused with potassium carbonate. The melt is dissolved in water, and the hot solution is precipitated by dilute hydrochloric acid, followed by a slight excess of ammonia. The earth acid is collected, rinsed into the fluoride solution, and the paper is washed with dilute hydrofluoric acid and discarded.

The solution is freed from excess acid by evaporation to low bulk in platinum. Assuming that 5 g. Ta_2O_5 were taken, the solution is diluted to 100 ml., heated to boiling, and treated during constant stirring with a hot solution of potassium fluoride. Theoretically, 5 g. Ta_2O_5 require 2.63 g. KF for the formation of K_2TaF_7 ; a little less than 3 g. of the salt is used. As potassium fluoride is not a usual reagent, potassium hydroxide (2.7 g.) may be dissolved in water (platinum crucible) and the cold solution slightly acidified with hydrofluoric acid.

The solution containing the crystalline precipitate of fluorotantalate is evaporated to about 60 ml., left to cool completely, and filtered by decantation through a rubber funnel into a bakelite dish. The felted mass of crystals is compressed with a strip of platinum or silver, washed four times with cold water (10 ml. portions), and rejected.

The filtrate and washings are returned to the platinum dish, and evaporated with 15 ml. of sulphuric acid (1 : 1) until strong white fumes are given off. The acid is cooled, diluted with water (which is used to wash down the inside of the dish), treated with 4 g. of bisulphate, and the evaporation is repeated. The mass is

heated until the sulphuric acid is expelled and a bisulphate melt is left. This is dissolved by heating in 100 ml. of saturated ammonium oxalate solution, and the liquid is transferred to an 800-ml. beaker. The solution (300 to 400 ml.), containing about 0.25 g. of Ta_2O_5 , is boiled and precipitated with 1 g. of tannin and 5 g. of ammonium chloride, etc., as under (a).

(c) *Meimberg's Colorimetric Method.*¹ Reference should be made to this process, of which I have no personal experience. The method is applied to the determination of niobium in potassium fluorotantalate. The precipitate is dissolved in hydrochloric acid containing a little hydrofluoric, and the liquid is evaporated until a copious precipitate of fluorotantalate has separated. The solution is left to cool, and the precipitate is collected and washed with cold dilute hydrofluoric acid. The filtrate is evaporated in a platinum dish, the residue is dissolved in strong hydrochloric acid, and the solution is reduced with tin for fifteen minutes in a Nessler tube. The colour is matched against a standard, which must be freshly prepared for each determination. The process applies to niobium contents of less than 0.1 per cent., and is stated to be accurate within 0.01 per cent. if 10 g. of material is used.

¹ *Z. angew. Chem.*, 1913, 26, 83.

CHAPTER XII

THE SEPARATION OF ZIRCONIUM, ALUMINIUM, URANIUM AND BERYLLIUM

Introduction

THE separation and determination of zirconium, aluminium, uranium, and beryllium complete the analytical scheme presented in Part II of this work.

It may be borne in mind that uranium is likely to be the most abundant member of Group B in earth-acid minerals. Zirconium also may be met with in substantial amounts, whilst aluminium and beryllium, if present, are always subordinate.

The process described below utilises cupferron for the determination of zirconium (§ 65). The bisulphate melt of the remaining oxides is treated with ammonium carbonate solution (§ 66), giving an insoluble aluminium-beryllium fraction and a soluble uranium-beryllium fraction. The solution of the latter is treated with potassium ferrocyanide, which precipitates uranium (§ 67); the beryllium in the filtrate is recovered and added to the aluminium-beryllium fraction, which is then resolved into its constituents by sodium carbonate fusion (§ 69). Minute quantities of beryllia are readily identified by the quinalizarin reaction (§ 70).

§ 65. Separation of Zirconium (and Hafnium) from Uranium, Aluminium and Beryllium by Cupferron

So far we have not made use of cupferron in any of the procedures described in Chapters VII to XI. The reagent is not sufficiently selective to effect separations in solutions containing more than a limited number of elements,¹ whilst for the joint recovery of earths from solution we give preference to tannin as being the cheaper, stabler, and, on the whole, more efficient group-reagent. In the analysis of tannin Group B, however, the use of cupferron offers decided advantages, a clean-cut separation of zirconium from uranium, aluminium and beryllium being brought about in a single treatment. Cupferron is most useful for mixtures in which zirconia preponderates. The procedure given below is that used and communicated to me by my collaborator, Mr. A. R. Powell.

¹ Cf. Lundell and Knowles, *J. Ind. Eng. Chem.*, 1920, 12, 344.

§ 65 ZIRCONIA : CUPFERRON PRECIPITATION

Procedure. The oxides of tannin Group B, obtained as described in § 51, are fused with 2 to 3 g. of potassium bisulphate, and the melt is dissolved in dilute sulphuric acid (4 per cent. by volume). The solution is filtered from a little silica into a 600-ml. beaker, and the filter is washed with 4 per cent. sulphuric acid. The cold solution (10° C.), occupying a bulk of 150 to 250 ml., is treated with a liberal amount of filter pulp, stirred, and precipitated gradually with an excess of freshly-made, filtered 6 per cent. solution of cupferron. The cupferron compound of zirconium is white, curdy, and flocculates on stirring. When precipitation is complete, further addition of reagent causes a momentary formation of a fine white precipitate which re-dissolves. After standing for a few minutes, the precipitate is collected by suction on a 9 or 11-cm. filter, and washed with 4 per cent. sulphuric acid containing a few drops of cupferron. When the washing is completed, the filter is sucked as dry as possible, transferred to a tared porcelain crucible, and gently ignited on an asbestos mat under a hood until completely charred. The ignition is completed at high temperature; after cooling, the precipitate is weighed as ZrO_2 . If substantial, it should be leached and again ignited and weighed.

The filtrate from the cupferron precipitate is boiled for fifteen minutes, then treated with nitric acid; boiling is continued until effervescence ceases and red fumes are no longer given off. The liquid is cooled, made slightly ammoniacal, and treated while boiling with filter pulp and a solution of 0.5 g. of tannin. After cooling for an hour, the liquid is filtered under suction; the precipitate is washed with slightly ammoniacal ammonium nitrate solution containing a few drops of tannin, and ignited in a silica crucible. (Further treatment: § 66.)

If the earth-acid mineral under investigation contains substantial amounts of thorium, the weighed zirconia precipitate should be tested for thorium by the oxalate method (§ 45). The small impurity of thorium thus found is derived from *HP*, which tends to occlude a little of this earth (§ 25, 7), and which has not been subjected to the operations described in Chapter VIII. Lundell and Knowles¹ have shown that a small admixture of thorium is precipitated more or less quantitatively with zirconia by cupferron.

§ 66. Separation of Uranium (Beryllium) from Aluminium by Ammonium Carbonate

The next step in the analysis of Group B—the resolution of the ternary mixture (U—Al—Be)—does not appear to have received much

¹ *J. Amer. Chem. Soc.*, 1920, 42, 1446.

attention in the literature. Uranium and beryllium share the property of forming soluble double alkali carbonates, and processes for the separation of uranium from aluminium, and of beryllium from aluminium, are based on the insolubility of aluminium hydroxide in carbonate solutions. For the separation of the three elements in the relative proportions in which they occur in earth-acid minerals (uranium preponderating over aluminium and beryllium, if present), I use the procedure about to be described, supplemented by those given in §§ 67 to 69. It effects the separation of uranium from small amounts of aluminium in one operation. Beryllium tends to distribute itself over the precipitate and the solution, but the purpose of the present procedure is to obtain the uranium free from aluminium; each of the two fractions will then be tested for beryllium.

In order to obtain a dense aluminium precipitate which filters well and does not occlude uranium, I treat the solid salts with ammonium carbonate solution. The operation is on a very small scale, hence, even if the precipitate was less dense, there would be next to no risk of loss of colloidal aluminium hydroxide as in a great bulk of solution.

Procedure. The mixed oxides recovered from the cupferron filtrate (§ 65) are fused with bisulphate, an excess of which should be avoided. The fusion is dissolved in 20 ml. of water, and the solution is filtered from a little silica. The filtrate is received in a squat 250-ml. beaker, neutralised with ammonia, and evaporated just short of complete dryness on a steam-bath. The residue is treated with 5 ml. of freshly-made 10 per cent. ammonium carbonate solution (which should prove an ample excess), and stirred with a glass rod to promote solution. A little warm water is added to dissolve the sulphates, and the solution, occupying a bulk of about 20 ml., is allowed to stand a few minutes at about 60° C. When cold, it is filtered through a 7-cm. paper containing a little pulp. The beaker is rinsed and cleaned with the help of a little pulp, cold water containing a few drops of ammonium chloride and carbonate being used as the wash-liquor.

The washed precipitate is ignited; if not perfectly white, it should be fused with a little bisulphate, and the above operations repeated. The alumina fraction is reserved pending the separation of uranium from beryllium (§ 67).

Determination of the Uranium. (a) If the amount of beryllia present is very small, the uranium may be determined in the yellow filtrate by acidification and vigorous boiling to expel the whole of the carbon dioxide, precipitation with carbonate-free ammonia and a liberal proportion of filter pulp, washing with ammonium nitrate solution, and ignition to U_3O_8 . The weighed precipitate should be tested, and the weight corrected, for silica and beryllia. The precipitate is fused with bisulphate, the mass

dissolved in water, and the silica filtered off, ignited, and weighed ; the filtrate is treated as in § 67.

(b) An alternative procedure for more substantial admixtures of beryllia consists in acidifying the yellow filtrate with sulphuric acid, boiling off carbon dioxide, and cooling. The liquid is treated with dilute ammonia until slightly turbid ; it is then cleared by very slight acidification with dilute sulphuric acid. The solution is now ready for the separation of uranium from beryllium (§ 67).

Using the above procedure on a mixture of 0.0100 g. Al_2O_3 , 0.0118 g. BeO , and 0.0685 g. U_3O_8 , I obtained after a single treatment a perfectly white alumina fraction weighing 0.0146 g. Hence about 40 per cent. of the beryllia was precipitated with the alumina.

§ 67. Separation of Uranium from Beryllium by Potassium Ferrocyanide

Schoeller and Webb (XXX.) have shown that the precipitation of uranium as ferrocyanide provides a clean-cut separation from beryllium in one operation in weakly acid sulphate solution, in which respects the procedure is superior to others, while the precipitant is a cheap, stable, and common reagent. Against this has to be set the disadvantage that iron is introduced into the solution, which necessitates another, though easier, separation. The difficulty of filtering the slimy uranyl ferrocyanide is easily and completely overcome by the use of filter pulp.

Procedure. The acidified uranium filtrate obtained in § 66 is treated in the cold with a cream of filter pulp and a fresh solution of 0.1 to 0.3 g. of potassium ferrocyanide ; the liquid is vigorously stirred, the precipitate blending with the fibre. The liquid is allowed to stand for about an hour, when the precipitate deposits completely, provided enough pulp has been added. The liquid is filtered through close-textured paper ; the matted pulp containing the red precipitate is returned to the beaker with 2 per cent. ammonium chloride solution, stirred up, returned to the filter, and the washing is completed. (Treatment of precipitate : § 68.)

The filtrate from the ferrocyanide precipitate is treated with a little filter pulp, made slightly ammoniacal, heated to boiling, and treated with 0.2 g. of tannin. The beryllium precipitate is left to settle, collected, washed with 2 per cent. ammonium nitrate solution, and ignited in a platinum crucible. (Further treatment : § 69.)

Our test separations of uranium from beryllium gave the following results (XXX.) :

Exp.	G. taken.		Found.		Error.	
	U ₃ O ₈	BeO	U ₃ O ₈	BeO	U ₃ O ₈	BeO
1	0·1320	0·0237	0·1325	0·0226	- 0·0005	- 0·0011
2	0·0406	0·0443	0·0409	0·0424	+ 0·0003	- 0·0019
3	0·1162	0·0206	0·1166	0·0208	+ 0·0004	+ 0·0002
4	0·0652	0·0512	0·0662	0·0506	+ 0·0010	- 0·0006

In Exps. 1 and 2, in which no tannin had been added in the beryllium precipitation, we accounted for the negative errors by re-treating the ammoniacal filtrates with tannin and a few drops of ammonia: the small precipitates thus obtained gave strong beryllium reactions with quinalizarin (§ 70).

The ferrocyanide method for the separation of uranium from beryllium provides an additional safeguard against the remote risk of low aluminium results due to loss of colloidal hydroxide in the ammonium carbonate method (§ 66): the minute amount of aluminium in question would accompany the beryllium into the filtrate from the uranyl ferrocyanide, and be recovered by precipitation with tannin and ammonia. For the separation of the bulk of the alumina from uranium, however, I do not feel safe in advocating the ferrocyanide procedure, as it gave low aluminium recoveries in two test separations.

§ 68. Determination of Uranium by Tannin Precipitation

The alternative procedure, (b), § 66, must be supplemented by the direct determination of uranium in the ferrocyanide precipitate. This is accomplished by decomposition of the precipitate, elimination of the relatively small amount of iron as sulphide from tartrate solution, and recovery of the uranium in the filtrate by tannin precipitation (XXV.).

Procedure. The filter containing the ferrocyanide precipitate (§ 67) is returned to the beaker and dissolved in strong sulphuric acid. The liquid is warmed and treated with small quantities of strong nitric acid until the organic matter has been destroyed. When cold, the acid is diluted with water, the liquid is treated with 2 g. of tartaric acid, 10 g. of ammonium chloride, and saturated with hydrogen sulphide. The iron is precipitated as sulphide by addition of excess of ammonia. After standing for some hours or overnight, the precipitate is filtered off, washed as usual, and rejected. The filtrate is acidified with acetic acid, boiled for the removal of hydrogen sulphide, made feebly ammoniacal, and precipitated while boiling with 1 g. of tannin and 5 g. of ammonium acetate. The dark-brown precipitate is collected, washed, and ignited as in § 13. The weight is normally excessive, due to contamination with silica. The weighed oxide

is therefore dissolved in strong nitric acid, the solution is evaporated to dryness, the residue taken up in hot water and a drop of acid and the insoluble matter is collected, washed, ignited and weighed. This weight is deducted from the gross weight, the difference representing U_3O_8 .

The quantitative precipitation of uranium by tannin from neutralised tartrate solution was studied by Schoeller and Webb (XXV.), who obtained the following results :

G. U_3O_8 taken.	Found.	Error.
0.0576	0.0578	+ 0.0002
0.0676	0.0678	+ 0.0002
0.0808	0.0809	+ 0.0001

§ 69. Separation of Alumina from Beryllia by Fusion with Sodium Carbonate

The last of the separations described in Part II of this work, viz., that of alumina from beryllia, is a much-discussed subject with a copious literature. I do not intend offering a choice of rival procedures, but will confine myself to a description of Wunder and Wenger's sodium carbonate fusion method,¹ as it is simplest in execution and as accurate as any other process. Moreover, fusion with sodium carbonate is a purification procedure for crude beryllia precipitates, as pointed out by Schoeller and Webb (XXX.). Beryllium hydroxide precipitated by ammonia occludes alkali if present, and if precipitated from sulphate solutions it carries down substantial amounts of sulphur trioxide, from which it cannot be freed by ignition and hardly so by re-precipitation. Fusion of such precipitates with sodium carbonate removes, not only sulphur trioxide and adsorbed alkali, but also elements forming soluble sodium salts in general, and alumina and minor quantities of silica in particular. We can, therefore, determine beryllium in sulphate solutions (*i.e.*, obtained by a bisulphate fusion) by ammonia or tannin precipitation, and fusion of the precipitate with sodium carbonate.

Procedure. The mixed precipitate obtained by ammonium carbonate (§ 66) is added to the platinum crucible containing the balance of the beryllia (§ 67). The oxides are fused with 2 to 3 g. of sodium carbonate for an hour or more at a temperature slightly above the melting-point of the salt. The melt is dissolved in 100 ml. of hot water in a porcelain basin, and the solution is filtered through a close-grained filter (Munktell No. 00) containing a small pad of filter pulp pressed into its apex. The precipitate is collected, washed with hot water, ignited strongly, and weighed as BeO . It usually contains a fraction of a mg.

¹ *Z. anal. Chem.*, 1912, 51, 470.

of ferric oxide, as indicated by its pink colour ; the pure oxide is white. The final treatment of the beryllia and its identification are described in § 70.

The alkaline filtrate from the beryllia, containing the alumina, is treated in known manner for its determination.

§ 70. Colorimetric Determination of Beryllium

Quinalizarin (1-2-5-8-tetrahydroxyanthraquinone) gives a fine corn-flower-blue lake with alkaline solutions of sodium beryllate. The useful and sensitive test for the identification and colorimetric determination of beryllium has been worked out by Dr. H. Fischer.¹ As the beryllia obtained in the preceding paragraph has been weighed, it is really unnecessary to determine it quantitatively at this stage ; but as a small correction for ferric oxide in the weighed beryllia is required, I consider it advisable to combine the determination of the iron with the certain identification of a rather infrequent and always subordinate constituent of earth-acid minerals by means of Fischer's test. The alkaline solution of the dye has a violet colour. The presence of aluminate is immaterial ; hence, even if aluminium had not been removed by sodium carbonate fusion, it could not be mistaken for beryllia in the test.

Procedure. Two solutions are required : (1) a 0.25*N* solution of sodium hydroxide, and (2) a 0.05 per cent. solution of the dye in 0.25*N* sodium hydroxide solution.

The weighed beryllia precipitate obtained in § 69 is fused with a small quantity of bisulphate, and the solution of the melt is treated with a moderate excess of the sodium hydroxide solution. The small precipitate of ferric hydroxide is mixed with a little filter pulp, collected, washed twice with water, dissolved in a little hydrochloric acid, and the iron in the solution is determined colorimetrically as thiocyanate. The quantity found is calculated to Fe_2O_3 and subtracted from the weight of the crude beryllia.

The alkaline filtrate from the iron precipitate is treated drop by drop with a freshly-made solution of the dye (*supra*), which produces a fine, pure blue colour if beryllium is present. The colour can be matched, if desired, against that of a standard containing a known amount of beryllium.

¹ *Z. anal. Chem.*, 1928, 73, 54.

PART III

THE APPLICATION OF TANNIN IN
GRAVIMETRIC ANALYSIS
QUALITATIVE ANALYSIS

CHAPTER XIII

GENERALITIES ON THE USE OF TANNIN AS A REAGENT

§ 71. Tannin as a Precipitant in Mineral Analysis

THE pure tannin of commerce is gallotannic acid. It is soluble in hot water to a colloidal suspension of negatively charged particles, and its use as a reagent is based on its faculty to precipitate positively charged sols of metallic hydroxides or other compounds by reciprocal flocculation. The precipitation is not a chemical reaction in a stoichiometric sense; hence the still obscure constitution of tannic acid and the fact that it may contain variable amounts of gallic acid and glucose are of no practical importance in mineral analysis.

The adsorption complexes obtained by precipitation with tannin are voluminous flocculent precipitates which filter well, especially under slight suction and when mixed with a little filter pulp. Upon ignition they leave the metallic oxides as soft, light powders, which readily attain constant weight and dissolve in a few minutes upon fusion with bisulphate.

§ 72. Importance of Tannin in the Analytical Chemistry of the Earths

Tannin has rapidly acquired paramount importance in the analysis of minerals and alloys containing earth-forming metals, and is absolutely indispensable in the analytical chemistry of tantalum, niobium and titanium. This is due to a combination of properties of which the following are the most important :

(1) *Tannin quantitatively precipitates every earth-forming and many other metals from tartrate solution* ; hence a general method for the separation of the sulphide-forming metals from the others consists in treating a tartrate solution with hydrogen or ammonium sulphide, or both in succession, and recovering the metals not precipitable as sulphides from the filtrate by precipitation with tannin.

(2) *Under specified conditions, tannin quantitatively precipitates tantalum, titanium and niobium from oxalate solution, the other earth-forming elements remaining in solution.* A quantitative separation of any or all of these metals from any or all of the non-precipitable elements can thus be achieved.

(3) *Certain hitherto impracticable analytical operations can be carried out with the aid of tannin.* Such are the quantitative separation of tantalum from niobium in any relative proportions, even on a mg.-scale, the separation of small amounts of earth acids from titania, and the quantitative determination of minute amounts of tungsten in solutions containing much alkali chloride.

(4) *A number of earth-forming elements and others yield tannin adsorption complexes of characteristic colour.* This property is of great importance in the analysis of elements most of which give white oxides and colourless solutions, not only as regards their detection and identification, but for the control of the quantitative separation processes.

All the above observations were made in the course of our "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates," the first paper on the quantitative application of tannin having been published in 1925 (IV.). Subsequently, L. Moser and his co-workers applied tannin in the analytical chemistry of beryllium, gallium, etc. (1927-30).

As far as I know, only one earlier reference to the use of tannin in quantitative analysis has been made in the literature. In 1905, R. E. Divine¹ recommended the addition of 2 to 6 ml. of 2.5 per cent. tannin solution in the precipitation of aluminium hydroxide by ammonia in order to coagulate the precipitate and facilitate filtration. This statement appears to have passed almost unnoticed. A short paper by Puran Singh,² entitled "Nickel tannates," appeared in 1914; it is of no analytical interest, the author endeavouring to prove, on quite inconclusive evidence, that nickel forms two definite tannates.

§ 73. State of Aggregation of Tannin Adsorption-complexes

The adsorptive capacity for tannin varies with the degree of dispersion of the metallic hydroxide. Thus, if the tannin suspension is added to a hydroxide precipitate after the latter has flocculated, the small surface of the denser aggregates of the hydroxide gel adsorbs a very limited amount of tannin; as a result, the bulk of the precipitate undergoes no appreciable increase, while its colour (if the complex is a coloured one) will be much paler than that of the more voluminous variety. If on the other hand the metallic hydroxide is precipitated from a hot tannin suspension in presence of an electrolyte, the small primary hydroxide particles at once adsorb those of the tannin sol, and the

¹ *J. Soc. Chem. Ind.*, 1905, 24, 111.

² *Ibid.*, 1914, 33, 172.

secondary aggregate formed is a voluminous adsorption-complex of high tannin content, and of vivid hue if coloured.

As a practical illustration, if niobic oxide is fused with potassium carbonate and the aqueous solution of the melt treated with excess of hydrochloric acid, a white precipitate of niobic acid is formed. If now the hot suspension is treated with tannin solution, the precipitate turns orange without increasing in bulk. If however the niobic oxide is fused with bisulphate and the melt is dissolved in a solution of ammonium oxalate, the boiling solution, on being treated with tannin and ammonium chloride and acetate, yields a voluminous precipitate of fine vermilion colour. Similar observations can be made with the tannin complexes of other elements.

Again, the tannin adsorption complexes of different elements differ in bulkiness. This increases, as we have seen, with the degree of dispersion, or stability, of the solution; hence the more unstable tantalum solutions, for example, being partly colloidal, furnish denser tannin precipitates than the stabler solutions of aluminium compounds.

§ 74. Classification of Tannin Procedures

We will now consider the conditions under which quantitative precipitations and separations by means of tannin can be effected. The presence of an *electrolyte* in adequate quantity, and precipitation from *hot* solution are necessary for satisfactory flocculation. The adjustment of the *acidity* is of the greatest importance in most cases, especially in the more delicate separation processes; this factor does not admit of general discussion at this stage, and must be dealt with in the next chapter, where the necessary directions will be given under the headings of the various elements or groups of elements. The most important factor, however, is the presence of a reagent which determines the course of the tannin reaction. In the table given below the first column gives a list of six such reagents, the neighbouring column containing the symbols of the elements which can be determined, recovered or separated by means of tannin and the corresponding reagent.

1. Mineral acid	W (§ 77). Ta, Nb (§ 78).
2. Acetate .	Ti (separation from other metals : § 79). Be (separation from other metals : § 80).
3. Tartrate .	U (§ 81). Ga (§ 82). Cu (§ 83). Al, Fe, Cr, Ga ; Ti, Zr, Hf, Th ; V, Nb, Ta ; U (§ 84).
4. Salicylate	Ti (§ 85).
5. Oxalate .	Group A : separation from Group B ; Ta from Nb (§ 86).
6. Ammonia	Group C : rare earths, Be, Mn (§ 87 ; 88).

The reagents in Column 1 are of two different kinds; they either affect the hydrogen ion concentration, and therefore the charges on the two kinds of particles (Nos. 1, 2, 6), or they act as complex formers (Nos. 3, 4, 5). The application of acetate in tannin procedures has been studied by Moser and others; that of the remaining reagents forms part of our investigations into earth-acid analysis.

§ 75. Serial Order of Precipitability of Certain Elements by Tannin from Oxalate Solution

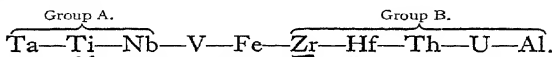
The most interesting applications of tannin in the analysis of earth-forming elements are the reactions taking place in oxalate solution (No. 5 in the table), as it is on them that certain hitherto most perplexing separations are based.

In the course of our researches we have been able gradually to establish a serial order of precipitability by tannin from oxalate solution. In the first place we worked out the separation of tantalum from niobium (IV.). Tantalic oxide is the least reactive of all the earths, and is therefore first in order of precipitability by tannin. We next demonstrated the interference of titania in the above separation procedure through partial co-precipitation with and consequent discoloration of the tantalum precipitate (XI.). The inference that titanium is therefore placed between tantalum and niobium in order of precipitability was fully confirmed during our researches on vanadium (XXXII.), which we were able to separate from tantalum and from titanium, but not from niobium, by the tannin process. This proves a serial order Ta—Ti—Nb—V; and as we have been unable quantitatively to separate either tantalum from titanium or niobium from vanadium by our procedure, we may generalise by saying that two neighbours in the series cannot be separated from each other by the tannin process, at least not without elaborate fractionation.

Turning to the separation of tantalum, titanium and niobium (Group A) from zirconium, aluminium, uranium, etc. (Group B) (XXIII.), a process described in Chapter IX, we found iron, when present in quantity, to be "a less tractable" member of Group B, as it reacts more readily with tannin than the other members of that group (see § 51, notes on Exp. 22). We therefore place iron next to vanadium in the series, and class them together as transitional elements because their precipitability is intermediate between that of Groups A and B: Ta—Ti—Nb—V—Fe'''.

Next to iron must be placed the three quadrivalent mem-

bers of Group B in increasing order of basicity, thus : Fe'''—Zr—Hf—Th. This part of the series has not been deduced from actual experimentation, but it must be conceded that the dioxide earths should be located between the fairly acidic Fe₂O₃ and the succeeding, more basic uranic oxide and alumina. These two oxides complete the series, probably in the order Th—U—Al. Chromium no doubt belongs here, but we will not complicate the series by its inclusion :



The presence of vanadium and iron would complicate the separation of Group A from Group B, described in Chapter IX, but iron (if present in substantial amounts) should be first eliminated as sulphide from ammoniacal tartrate solution, while vanadium has not so far been met with in earth-acid minerals. Methods for the separation of vanadium from titanium, niobium and tantalum are given in § 78.

The precipitation intervals between the members of Group B are probably very small, but it is a tempting proposition, in default of simple methods, to essay the separation of zirconium from hafnium by fractional tannin precipitation. I have on one occasion separated vanadium from aluminium by fractional tannin precipitation in oxalate solution.

CHAPTER XIV

QUANTITATIVE DETERMINATION AND SEPARATION METHODS BASED ON TANNIN PRECIPITATION

§ 76. Alphabetical Index

THIS chapter presents the analytical tannin procedures published from 1925 to the middle of 1936. The order in which the processes are described is that adopted in § 74 (see table). The alphabetical index below will facilitate reference to the methods given in this chapter.

Aluminium. Determination, § 84 (e), § 87 (a); separation from iron, § 84 (e).

Beryllium. Determination, § 87 (b); § 88 (b). Separation from aluminium, iron, chromium, thorium, vanadium, titanium, zirconium, tin, § 80.

Chromium. Precipitation, § 84 (d).

Copper. Determination, § 83.

Gallium. Determination, § 82 (a); separation from zinc, etc., § 82 (b).

Iron. Precipitation, § 84 (d).

Manganese. Precipitation, § 88 (a).

Niobium. Separation from tantalum, § 86 (b).

Niobium and Tantalum. Determination, § 84 (b); in wolframite, § 78 (c). Separation from tannin group B, § 86 (a); from titanium and zirconium, § 78 (a); from vanadium, § 78 (b). Micro-determination, § 86 (d).

Rare Earths. Determination, § 87 (c); § 88 (c).

Tantalum. Separation from niobium, § 86 (b); see also *Niobium and Tantalum*.

Thorium. Determination, § 84 (b).

Tin. Precipitation, § 80 (h).

Titanium. Determination, § 84 (a), (b). Separation from tannin group B, § 86 (a); from iron, aluminium, chromium, nickel, cobalt, zinc, manganese, phosphoric acid, § 79. Recovery from salicylate solution, § 85.

Tungsten. Determination, § 77 (a). Separation from uranium, aluminium, beryllium, § 77 (b).

Uranium. Determination, § 81 (a), § 84 (c). Separation from titanium, § 81 (b).

Vanadium. Determination, § 84 (c). Separation from niobium and tantalum, § 78 (b); from titanium, § 86 (c).

Zirconium. Determination, § 84 (b).

1. PROCEDURES CARRIED OUT IN MINERAL ACID SOLUTION

The elements affected by these procedures are tungsten, tantalum and niobium, the hydroxides of which—the metallic acids—are insoluble in dilute mineral acid; and titanium, which is precipitated by antipyrin from an acid sulphate solution in presence of an excess of tannin.

§ 77. Tungsten

(a) *Determination.* The precipitation of small quantities of tungstic acid by means of tannin, with addition of cinchonine as a collecting agent (VII.), has already been described in § 37. After numerous applications, I consider the procedure to be accurate and by far the most convenient for determining small quantities of the element.

Antipyrin may be substituted for cinchonine as a collecting agent, as shown by Moser and Blaustein.¹ Their misinterpretation of the rôle of cinchonine in our procedure, and our refutation of their criticism, are recorded in § 37.

(b) *Separation from Uranium, Aluminium and Beryllium.* If the alkaline tungstate solution submitted to the tannin-cinchonine method (§ 37) contains any sodium uranyl carbonate, sodium aluminate, or sodium beryllate,² the tannin complexes of these metals dissolve upon acidification of the solution with hydrochloric acid. When the tungsten precipitate has been filtered off, the uranium, aluminium and beryllium may be recovered from the filtrate by ammonia precipitation and ignition of the precipitate (*cf.* § 38).

§ 78. Niobium and Tantalum

(a) *Separation from Titanium and Zirconium.* The insolubility of the tannin adsorption complexes of niobium and tantalum in dilute sulphuric acid is applied in the separation of the earth acids from titania and zirconia by means of the pyrosulphate-tannin method (XV.), fully described in § 59.

(b) *Separation from Vanadium.* As niobium cannot be separated from vanadium by tannin in oxalate solution (§ 75), Schoeller and Webb (XXXII.) have worked out the following

¹ *Monatsh. Chem.*, 1929, **52**, 351.

² Moser and Singer, *ibid.*, 1927, **48**, 686.

combination procedure for the quantitative separation of vanadium from niobium and tantalum.

Procedure. The mixed oxides are fused with bisulphate, the product is dissolved in tartaric acid solution, and the liquid is boiled with strong hydrochloric acid (tartaric hydrolysis, § 11). The precipitate is free from vanadium.

The filtrate is neutralised with ammonia and boiled with tannin and ammonium acetate (§ 84 (c)); the blue-black precipitate containing the vanadium and the minor earth-acid fraction is ignited in a silica crucible.

The ignited tannin precipitate is fused with a little bisulphate, and the melt is extracted in the crucible with a warm 1 per cent. tannin solution in 2.5 per cent. sulphuric acid (pyrosulphate-tannin method, as under (a) above). After an hour's digestion on a steam-bath, the solution is transferred to a small beaker and treated with a drop or two of cinchonine hydrochloride solution; this, by producing a tannin precipitate, induces complete flocculation of the niobium-tannin complex. After standing in the cold for a few hours the solution is filtered, the earth-acid precipitate is washed with acidulated ammonium chloride solution, and ignited together with the major fraction.

The filtrate from the last treatment contains the vanadium; it is approximately neutralised with ammonia, treated with ammonium acetate, boiled and precipitated with tannin. The black precipitate is washed with ammonium nitrate solution and ignited to V_2O_5 , which should be corrected for silica by fusion with bisulphate and solution in dilute sulphuric acid. It is advisable, in view of possible positive errors (Exp. 1) to check the vanadium result by a volumetric determination in the filtrate from the silica.

Two tests (XXXII.) by the above method gave the following results:

Exp.	G. taken.		Found.		Error.	
			M_2O_5	V_2O_5	M_2O_5	V_2O_5
1	Ta_2O_5 0.2010	V_2O_5 0.0444	0.2011	0.0457	+ 0.0001	+ 0.0013
2	Nb_2O_5 0.2062	„ 0.0416	0.2057	0.0419	- 0.0005	+ 0.0003

(c) *Determination of Niobium and Tantalum in Wolframite.* Method of J. A. Tschernichow and M. P. Karsajewskaja.¹ This method, recommended for mineralogical and geochemical work, is based on the procedures presented in this monograph.

The finely ground mineral (10 g.) is attacked with hydrochloric acid, the solution is evaporated, boiled with nitric acid and diluted,

¹ *Z. anal. Chem.*, 1934, 98, 97.

and the yellow residue is collected and washed. The tungstic acid is dissolved in a mixture of 40 ml. of 10 per cent. ammonia and 20 ml. of saturated ammonium nitrate solution. The residue from the extraction is ignited and again submitted to the above process. The ignited residue from the second extraction is treated with hydrofluoric and sulphuric acids, evaporation with the latter acid is repeated, and the almost dry residue is digested with 10 per cent. hydrochloric acid. The liquid is made slightly ammoniacal, and the precipitate (containing the whole of the earth acids) is collected, washed with ammonium nitrate, ignited and fused with bisulphate. The melt is dissolved in tartaric acid, and the solution is freed from the metals of the hydrogen sulphide and ammonium sulphide groups. The filtrate is treated with cupferron and the ignited precipitate of impure pentoxides is weighed.

Two small portions (0.001 to 0.005 g.) are weighed off and tested colorimetrically, the one for titania, the other for tungstic oxide. If the latter preponderates, it is separated from the earth acids in the bulk of the precipitate by bicarbonate hydrolysis (§ 3); the earth-acid precipitate is freed from titania, if necessary, by the pyrosulphate-tannin method (§ 54). If titania preponderates, it is first removed by the same process, and the tungstic oxide next by bicarbonate hydrolysis. The separation of tantalum from niobium in the purified pentoxides is effected by the tannin method (§ 61). The tantalum and niobium fractions are tested colorimetrically for titania (§ 58) and tungstic oxide (*infra*).

The colorimetric determination of tungsten in the pentoxides (0.003 to 0.01 g.) is carried out by fusion with 1.3 g. of sodium carbonate, solution of the melt in 15 ml. of warm water, filtration if necessary, and dilution to 50 ml. Twenty ml. are pipetted into a 50-ml. flask, treated with 2.5 ml. of 25 per cent. potassium thiocyanate solution and made up to the mark with a solution of 10 g. of stannous chloride in 90 ml. of strong hydrochloric acid. The colour is matched after 45 to 60 minutes against those of a standard scale prepared from a sodium tungstate solution (0.0002 g. WO_3 per ml.), diluted with 0.5*N* sodium carbonate solution to 20 ml. and treated exactly like the unknown solution; standards and assay should be done at the same time.

§ 79. Titanium. Separation from Iron, Aluminium, Chromium, Nickel, Cobalt, Zinc, Manganese and Phosphoric Acid

Method of Moser, Neumayer and Winter.¹ The sulphate solution (maximum content, 0.1 g. TiO_2) is neutralised with

¹ *Monatsh. Chem.*, 1930, 55, 85.

ammonia and acidified with strong sulphuric acid (10 ml.); 40 ml. of 10 per cent. tannin solution are added, and water to a total bulk of 400 ml. The cold solution is stirred and treated with 20 per cent. antipyrin solution, which produces a flocculent orange-red precipitate; excess of reagent is indicated by the formation of a white, curdy precipitate. The liquid is now boiled and 40 g. of ammonium sulphate are added. After rapid cooling with frequent agitation, the precipitate is collected under slight suction and washed with a solution containing 5 per cent. by weight of sulphuric acid, 10 g. of ammonium sulphate, and 1 g. of antipyrin. Complete precipitation is proved by a white precipitate in the filtrate upon dropwise addition of antipyrin solution. The precipitate is dried, then cautiously charred in a platinum dish, finally ignited over a Teclu burner, extracted with acidulated water, collected on a small filter, again ignited, and weighed as TiO_2 .

The determination of the metals in the filtrate from the titanium precipitate is difficult, as the destruction of the antipyrin cannot be effected by wet methods.

2. PROCEDURES CARRIED OUT IN ACETATE SOLUTION

These comprise methods for the separation of beryllium from a number of metals, and for the separation and determination of gallium, by Moser and his co-workers. Procedures for the determination of uranium and copper have also been published.

§ 80. Beryllium

(a) *Separation from Aluminium.* Method of Moser and Niessner.¹ This is based on the precipitation of the aluminium-tannin complex from acetate solution, in which beryllium remains dissolved.

The hot, feebly acid sulphate solution (500 ml. for less, 600 to 800 ml. for more, than 0.1 g. Al_2O_3) is treated with hot reagent (a cold-saturated solution of ammonium acetate containing 3 g. of tannin per 100 ml.) during agitation. After two minutes' boiling, the precipitate is left to settle, and complete precipitation tested for with a few drops of reagent. After cooling, the precipitate is collected on a filter, washed with warm 5 per cent. ammonium acetate solution, dried, ignited in platinum, and evaporated two to three times with nitric acid. After strong ignition it is weighed as Al_2O_3 . If this exceeds 0.06 g., the voluminous tannin precipitate must be collected by suction in a glass crucible,

¹ *Monatsh. Chem.*, 1927, 48, 113.

washed as before, and dissolved in the covered crucible in nitric acid (1 : 3). The solution is received in a tall beaker, boiled, and treated with fuming nitric acid until the tannin is destroyed ; the solution is precipitated with ammonia as usual.

The filtrate from the aluminium precipitate is likewise oxidised with nitric acid and the beryllia is precipitated with ammonia. (Tannin precipitation : § 87.)

The method of Moser and Niessner has been criticised by Mitchell and Ward¹ in the following words : " We did not obtain satisfactory separations by the method of Moser and Niessner, possibly owing to insufficiently definite specification of the acidity conditions in their description." On the strength of my experience in the analysis of beryl I share the views of Mitchell and Ward, and have adopted Wunder and Wenger's process (§ 69) as the simplest one. At the same time, precipitation by tannin should be used for the separation of small amounts of alumina from much beryllia, the ignited aluminium precipitate being submitted to fusion with sodium carbonate.

(b) *Separation from Iron.*² The neutral solution, containing iron as ferric salt, is treated with ammonium acetate (30-40 g.), ammonium nitrate (20-25 g.), water to a bulk of 400-500 ml., and 1.5 ml. of 80 per cent. acetic acid per 100 ml. The solution is boiled, stirred and completely precipitated with 10 per cent. tannin solution. A few drops of hydrogen peroxide added before precipitation prevent slight reduction to ferrous salt. The precipitate is collected (the filtrate should be yellow-brown, not mauve), washed, dissolved in a few ml. of hot dilute sulphuric acid, and the filter washed to neutral reaction. The solution is nearly neutralised with ammonia, partial precipitation taking place, and the precipitation is repeated. The precipitate is collected, washed free from sulphate with hot ammonium nitrate solution, dried, and ignited to Fe_2O_3 . The combined beryllium filtrates are precipitated with excess of ammonia.

(c) *Separation from Chromium.*³ The procedure is the same as for iron (b) ; the solution should contain 2 per cent. of free acetic acid. Double precipitation is prescribed.

(d) *Separation from Thorium.*³ The white thorium precipitate is insoluble in 2 to 2.5 per cent. acetic acid. Double precipitation is required, the procedure being the same as for iron.

(e) *Separation from Vanadium.*³ The neutral solution of alkaline vanadate and beryllium salt (400-500 ml.) is treated with

¹ *Modern Methods in Quantitative Chemical Analysis*, London, 1932, p. 43.

² Moser and Singer, *Monatsh. Chem.*, 1927, **48**, 673.

³ Moser and Singer, *loc. cit.*

20 g. of ammonium acetate and 30 of nitrate, and 2.5 ml. of 80 per cent. acetic acid per 100 ml., boiled, and precipitated with 10 per cent. tannin solution (10 parts of tannin to one of V_2O_5). After short boiling, the voluminous deep-blue precipitate is collected and washed with 10 per cent. ammonium acetate solution. After ignition and nitric-acid treatment, it is heated till fused, and weighed as V_2O_5 . The filtrate has a green tint, but vanadium cannot be detected therein by known reactions.

(f) *Separation from Titanium.* The titanium complex being insoluble at higher acid concentration, a single precipitation suffices. The cold solution is treated with ammonia to incipient cloudiness, ammonium acetate (10 g.) and nitrate (20 g.), and 20 to 25 ml. of acetic acid; it is boiled, stirred, and the titania precipitated with about 10 times its weight of tannin. After short boiling the red precipitate is collected, washed with 10 per cent. acetic acid containing a little ammonium nitrate, and ignited to TiO_2 .

(g) *Separation from Zirconium.*¹ The white tannin precipitate is insoluble in acetic, and even in hydrochloric acid (1:20). The procedure is the same as for titanium (f); if the solution has not been neutralised to cloudiness, precipitation from the boiling liquid is more gradual.

(h) *Separation from Tin.*² Stannic sulphide adsorbs beryllium, hence tannin separation is recommended. The strongly acid, boiling chloride solution is treated with 5 ml. of 10 per cent. tannin solution, and 10–20 g. each of ammonium acetate and nitrate. The boiling solution becomes turbid, and the precipitate gradually flocculates; after one hour's heating on the water-bath, the tin adsorption-complex is completely precipitated. The precipitate is collected and washed with hot ammonium acetate solution containing a little tannin. If more than 0.2 g. of tin is present, the precipitate is dissolved in hot, strong hydrochloric acid, and the operations repeated. After being dried, the precipitate is ignited gradually, finally over a blast burner, and weighed as SnO_2 . In all the preceding separations the beryllia is precipitated in the filtrates by tannin and ammonia.

(i) *Separation from all the preceding Metals.* Moser and List³ state that tannin precipitation from acetate solution provides the means for separating beryllium from all the metals listed under (a) to (g), but it must be pointed out that they give no additional directions for separating beryllium from more

¹ Moser and Singer, *loc. cit.*

² Moser and List, *Monatsh. Chem.*, 1929, 51, 1133.

³ *Loc. cit.*

than one of the metals under discussion, and that no test analyses of oxide mixtures other than binary ones figure in the three papers cited. The method for the separation of iron from beryllium has been criticised by Dixon,¹ who states that it is liable to lead to co-precipitation of beryllium at the reduced acidity required for the complete precipitation of the iron. One element overlooked by Moser and List in their general scheme is uranium, which accompanies beryllium in a number of reactions, and is precipitated by tannin from neutralised acetate solution (§ 81), when co-precipitation of beryllium is almost certain to occur. The proposed general separation method might yield serviceable results by a process of fractional precipitation or re-precipitation, but in my opinion fresh experimental work is required to work out such a method.

§ 81. Uranium

(a) *Determination.* Das-Gupta² determines uranium by treating the neutral or faintly acid solution with fresh 2 per cent. tannin solution (2 ml. per 0.012 g. U), boiling, stirring and adding ammoniacal 10 per cent. ammonium acetate solution till the precipitate flocculates and the liquid clears. Liberal addition of ammonium salt promotes flocculation. The precipitate is collected and washed with slightly ammoniacal ammonium nitrate solution. If fixed alkali salts are present, the precipitate is to be washed by decantation with several portions of the same wash-liquor. The wet precipitate is ignited to U_3O_8 .

The tannin precipitate is not soluble in alkali carbonate, but soluble in dilute mineral, as well as excess of acetic acid. For small amounts of uranium, the method is more reliable than the usual ammonia precipitation method, in which the presence of carbonate in the precipitant leads to low results.

(b) *Separation from Titanium.*³ The feebly acid solution of the two metals (300–400 ml.) is treated with 30–40 ml. of glacial acetic acid, 10 g. of ammonium acetate and 15 to 20 of nitrate, boiled, and precipitated with excess of 10 per cent. tannin solution. The titanium precipitate is collected, washed with 10 per cent. acetic acid containing a little ammonium nitrate, ignited strongly, and weighed.

The filtrate containing the uranium is evaporated twice to dryness with nitric acid, the residue is dissolved in water, and the uranium is precipitated with ammonia.

¹ *Analyst*, 1929, 54, 268.

² *J. Indian Chem. Soc.*, 1929, 6, 763.

³ Moser, Neumayer and Winter, *loc. cit.*

§ 82. Gallium

(a) *Determination.* Method of Moser and Brukl.¹ Gallium hydroxide is gelatinous like aluminium hydroxide, and more soluble in ammonia than the aluminium precipitate; the presence of ammonium salts increases the solubility. The precipitation of basic gallium acetate is quite incomplete: a large excess of ammonium acetate may prevent the precipitation altogether. Moser and Brukl recommend tannin as the best and most sensitive precipitant for gallium (sensitiveness, 1 : 5,000,000).

The boiling, weakly acid acetate solution, containing 2 per cent. of ammonium nitrate, is stirred and treated drop by drop with a 10 per cent. solution of tannin till precipitation is complete: 10 parts of tannin suffice as a rule, but for minute amounts of gallium the tannin should be not less than 0.5 g., otherwise the precipitate does not deposit readily. It is very bulky, hence with more than 0.1 g. of Ga_2O_3 it is of inconvenient size; if a large amount of gallium is to be precipitated, the bulk may be obtained as basic acetate, and the balance in the filtrate by tannin. The precipitate is washed with hot water containing a little ammonium nitrate and a few drops of acetic acid. Filter and precipitate are dried and ignited in porcelain to Ga_2O_3 , which is weighed. Ammonium chloride should not be used in the washing, as gallium chloride is volatile.

(b) *Separation from Zinc.*² The above precipitation procedure permits of the accurate separation of gallium from zinc (its most important mineral associate), nickel, cobalt, manganese, cadmium, beryllium and thallium. The weakly acid (1 per cent. acetic) solution is treated with ammonium acetate and 2 per cent. of ammonium nitrate, boiled, and precipitated with tannin as described above. The precipitate is dissolved in hot dilute hydrochloric acid, and the precipitation is repeated.

§ 83. Copper

Darbinian and Kankanian³ have found that copper is quantitatively precipitated by tannin from acetate solution; the precipitate is chestnut-brown. The warm solution is treated with about 1 g. of ammonium acetate, and drop by drop with 25 ml. of 2 per cent. tannin solution, and left for a few minutes on the water-bath. The precipitate is collected, washed with hot water, ignited, dissolved in nitric acid, and the copper is deter-

¹ *Monatsh. Chem.*, 1928, 50, 657.

² Moser and Brukl, *loc. cit.*

³ *Z. anal. Chem.*, 1934, 99, 29.

mined iodimetrically. The precipitation is not quantitative from ammoniacal solution, the precipitate being more or less soluble according to the ammonia concentration.

3. PROCEDURES CARRIED OUT IN TARTRATE SOLUTION

§ 84. Quantitative Precipitation of Aluminium, Iron, Chromium, Titanium, Zirconium, Thorium, Vanadium, Niobium, Tantalum and Uranium from Neutral Tartrate Solution

In the foregoing analytical procedures carried out in mineral or acetic acid solutions, most of the reactions that take place are familiar to the analyst, as they consist in the precipitation of a hydrated oxide or basic salt (*viz.*, acetate). Adsorption of tannin by the precipitate takes place either at the moment of its formation in a highly disperse state, or after flocculation.

On the other hand, the reactions underlying the tannin methods about to be described are still quite obscure. In these the precipitant acts on solutions containing an organic compound capable of preventing the normal reactions of the metals affected. No satisfactory explanation for the interference of organic hydroxy-acids with the precipitation of metals by ammonia, etc., has yet been advanced, although Berzelius used tartaric acid for this purpose more than 100 years ago.¹ It is convenient, and no doubt correct, to speak of such solutions as containing organic complexes, as the metal is held in such a way as to resist the precipitating action even of caustic alkalis. Yet such a comparatively inert substance as tannin, dissolving in water to a colloidal solution, is capable of precipitating metals from the solution of their organic complexes. I am inclined to assume that organic acids and metals are capable of forming complex compounds giving molecular aggregates of considerable size, not far removed from that of the highly disperse tannin particles. The size of the molecules renders them susceptible to tannin precipitation by mutual flocculation. Further, the complexity of the molecule increases with progressive neutralisation of free acid by ammonia (as instanced by the colour of the ferric tartrate complex, which is most intense near the neutral point). In accordance with this view, precipitation by tannin should be more complete in neutral than in acid solution, which is actually the case. Increased addition of a strong acid (*e.g.*, hydrochloric), on the other hand, leads to decrease in molecular complexity, resulting eventually

¹ *Pogg. Ann.*, 1825, 4, 3.

at boiling heat and a sufficiently high acid concentration in the formation of the metallic chloride (yellow solution in the case of ferric salts) or, if this is incapable of existence in aqueous solution, to the precipitation of the hydrated oxide (precipitation of the metallic acids by "tartaric hydrolysis").

These views may be erroneous, but they fit in fairly well with the facts observed in the course of our investigations, and may serve, *faute de mieux*, as a provisional working hypothesis (see also § 85).

Of all the metals we have investigated, tungsten is the only one not precipitated by tannin from tartrate or oxalate solution, though in presence of preponderating quantities of other metals, partial precipitation takes place (§ 40). The behaviour of tungsten does not appear to me to invalidate the views here expressed when its strong power of heteropolyacid-formation is borne in mind. It is only necessary to make the reasonable assumption that, in accordance with its marked individuality, tungsten forms complexes of a peculiar type with organic acids, and of greater stability than those of the other metals.

(a) *Titanium*. Quantitative precipitation of a metal by tannin from tartrate solution was first observed by Schoeller and Powell (XI.), who found that titania can be completely recovered in this manner after careful neutralisation of the solution. Thornton's monograph¹ includes the tannin reaction amongst the qualitative tests for titanium, with the remark that "citric acid delays but does not prevent formation of the precipitate."

(b) *Titanium, Zirconium, Thorium, Niobium, Tantalum*. The observation of Schoeller and Powell (a) was investigated at greater length by Schoeller and Webb (XVII.), and the method evolved by them was extended to tantalum, niobium, zirconium, thorium and aluminium. It involved careful neutralisation of the solution with ammonia after addition of the precipitant. I have since found that it is more convenient to expel free ammonia by boiling, as described below, and then to precipitate the earths with tannin, ammonium acetate being added as a neutralising agent.

Procedure. The solution should contain 20 to 30 ml. of hydrochloric acid, or its equivalent in ammonium chloride; if it contains ammonium sulphide, it is acidified with hydrochloric acid and boiled until hydrogen sulphide is removed. The acid liquid is made slightly ammoniacal, and boiled for some time for the expulsion of free ammonia. The boiling solution is treated

¹ *Titanium*, New York, 1927, p. 58.

with tannin (20 times the weight of the oxides present) and 5 g. of ammonium acetate, and boiled for a few minutes. After being allowed to stand hot for half an hour, the solution is filtered, under slight suction if necessary, and the precipitate is treated as in § 13 (lixiviation and silica correction).

The following results are reproduced from Schoeller and Webb's paper (XVII.). The weights of the precipitates before and after purification are entered under gross and net, respectively.

G. taken.	Found.			Error.
		Gross.	Net.	
Ta ₂ O ₅	0.0052	0.0061	0.0054	+0.0002
Nb ₂ O ₅	0.0073	0.0084	0.0071	-0.0002
(Ta,Nb) ₂ O ₅	0.0178	0.0205	0.0175	-0.0003
ZrO ₂	0.0054	0.0073	0.0052	-0.0002
TiO ₂	0.0263	0.0283	0.0265	-0.0002
„	0.0208	0.0234	0.0211	+0.0003
„	0.0258	0.0280	0.0249	-0.0009
„	0.0228	0.0242	0.0221	-0.0007
ThO ₂	0.0210	0.0227	0.0209	-0.0001
„	0.0231	0.0246	0.0229	-0.0002
(0.0212 ZrO ₂ + 0.0133 M ₂ O ₅ + 0.0123 ThO ₂)	0.0468	0.0492	0.0467	-0.0001
(0.0236 ZrO ₂ + 0.0131 M ₂ O ₅ + 0.0123 TiO ₂)	0.0490	0.0518	0.0484	-0.0006

(c) *Uranium and Vanadium.* The precipitation of uranium (XXV.) and vanadium (XXXII.) by tannin from neutral tartrate solution was studied by Schoeller and Webb. The procedure is the same as that described under (b) above. The determination of uranium and some of our results have been given in § 68; the recovery of vanadium from tartrate solution forms a step in our method for the separation of vanadium from tantalum and niobium (§ 78 (b)).

(d) *Iron and Chromium.* In the processes described in this book, iron is normally removed as ferrous sulphide from the tartrate solution prior to the precipitation of the earths by tannin; but if present it is quantitatively precipitated, betraying its presence, even in small amounts, by a pale to deep mauve discoloration of slightly coloured precipitates (such as the tantalum complex). The precipitation of chromium, which gives a greenish complex, has given serviceable results in the analysis of a few minerals and alloys.

(e) *Aluminium; separation from Iron in Ore Analysis* (XVII.). The separation of small quantities of aluminium from much

iron is a proposition frequently encountered in ore analysis. Precipitation of the alumina by thiosulphate is a process of questionable value; conversion into soluble sodium aluminate is preferable, but re-treatment of the iron precipitate is indicated. Determination by difference, after volumetric determination of the iron in the weighed mixed oxides, is wrong in principle because the subordinate constituent should actually be determined. Precipitation of ferrous sulphide from ammoniacal tartrate solution is an accurate process, and the tannin method obviates destruction of the tartaric acid prior to the precipitation of the alumina.

Procedure. The acid solution is treated with 2 to 3 g. of tartaric acid and 10 g. of ammonium chloride, and reduced with hydrogen sulphide. Addition of an excess of ammonia precipitates ferrous sulphide. The precipitate is allowed to settle for some hours or overnight. A loose filter containing filter pulp may be used; the filtrate should be pale yellow, not greenish. Washing is effected with dispatch; the wash-liquor should contain ammonium sulphide and nitrate. I prefer to ignite the iron precipitate, dissolving it in strong hydrochloric acid, reducing with stannous chloride, and titrating with permanganate. The filtrate from the ferrous sulphide is boiled with hydrochloric acid, neutralised with ammonia, and precipitated hot with excess of tannin followed by ammonium acetate; it is unnecessary to neutralise the solution as closely as for titanium and zirconium (*b*).

The coloration of the precipitate sometimes discloses an unexpected constituent: a yellow colour indicates titanium; pale blue, a small admixture of vanadium. The tannin precipitate is collected, washed, ignited and weighed.

Test separations by Schoeller and Webb (XVII.) gave the following results:

Exp.	Fe ₂ O ₃			Al ₂ O ₃		
	G. taken.	Found.	Error.	G. taken.	Found.	Error.
1	0.1131	0.1140	+ 0.0009	0.0066	0.0074	+ 0.0008
2	0.0954	0.0956	+ 0.0002	0.0114	0.0116	+ 0.0002
3	0.0764	0.0768	+ 0.0004	0.0079	0.0081	+ 0.0002
4	0.1108	0.1103	- 0.0005	0.0024	0.0025	+ 0.0001

The procedure has been in regular use for a number of years, giving great satisfaction as a routine method.

(*f*) *Gallium*¹ can be separated from iron like aluminium (*e*).

¹ Moser and Brukl, *loc. cit.*

4. PROCEDURE CARRIED OUT IN SALICYLATE SOLUTION

§ 85. Titanium

The oxalate-salicylate method for the separation of titania from the earth acids (§ 55) includes a step in which the titania is recovered from the salicylate solution by precipitation with tannin and ammonium acetate. The procedure is referred to here on account of its theoretical interest in connection with the discussion presented in § 84. Titanium is known to form complexes with several organic orthohydroxy-compounds.¹ Titanyl-salicylic acid is not of a very high order of stability, as it is decomposed by ammonia, hydrated titanic oxide being precipitated. When treated with tannin and ammonium acetate, the boiling, yellow to orange solution of titanylsalicylic acid gives a red precipitate of the titanium-tannin complex; the precipitation of the titania is quantitative.

Rosenheim and Sorge¹ have prepared a deeply-coloured complex of titanium and pyrocatechol (α -dihydroxybenzene), the stability of which is so marked that precipitated titanic acid dissolves completely in a boiling, ammoniacal pyrocatechol solution. I argued that this complex, which is stabler and more deeply coloured than titanylsalicylic acid (due to pyrocatechol containing *two* OH groups), may nevertheless be precipitable by tannin, for reasons indicated in § 84. This was verified by the following experiment.

Titania was fused with bisulphate, the solution of the melt was precipitated with ammonia, and the suspension was boiled with ammoniacal pyrocatechol solution. The boiling orange-red solution was treated with tannin, the titanium-tannin complex flocculating on addition of ammonium chloride. The titania content of the precipitate was confirmed by ignition, fusion with bisulphate, and identification of the titanium by hydrogen peroxide.

5. PROCEDURES CARRIED OUT IN OXALATE SOLUTION

§ 86. Paramount Importance of Tannin in Earth-Acid Analysis

These procedures form the most important application of tannin in the analysis of the earth-forming elements, as they enable us to analyse materials containing the earth acids as well

¹ Rosenheim and Sorge, *Ber.* 1920, 53, 937.

as other earths as a matter of routine and with a precision which, only a few years ago, was still regarded as unattainable. The procedures carried out in oxalate solution are :

(a) The separation of tannin group A (tantalum, titanium, niobium) from tannin group B (zirconium, uranium, aluminium, beryllium). This process is fully discussed in Chapter IX.

(b) The separation of tantalum from niobium. A detailed description of this important process is given in Chapter XI, § 61.

In the course of a physico-chemical study of the complex acids of tantalum and niobium, Britton and Robinson¹ applied electrometric investigation to solutions of the oxalo-earth acids in presence of tannin under the conditions of the tannin separation method. They conclude that the control of pH is of no service in effecting the separation ; the need for fractional precipitation is recognised by them, as well as the method of controlling the operation by observation of the coloration of the tannin precipitates.

(c) *Separation of Titanium from Vanadium.* The literature on this separation is scanty. Fusion of the mixed oxides with sodium carbonate and potassium nitrate produces soluble alkali vanadate and insoluble titan oxide ; treatment of a solution with sodium hydroxide in excess has the same effect.²

The tannin separation of the two elements, worked out by Schoeller and Webb (XXXII.), is a special case of the group separation noticed under (a) above. The technique is the same, but we found it necessary to omit the neutralisation, prior to tannin precipitation, of the oxalate solution with dilute ammonia, as this produced an immediate cloudiness requiring an undue amount of acid for its removal.

Procedure. The mixed oxides (0.25 g.) are fused with 3 g. of potassium bisulphate, the fusion being continued until most of the pyrosulphate is decomposed, as shown by the separation of crystals of neutral sulphate. The cold melt, which is more or less orange according to the quantity of vanadium present, is dissolved in hot, saturated ammonium oxalate solution (60–75 ml.). The crucible is rinsed with a little water ; the solution is diluted with 75 ml. of saturated ammonium chloride solution, boiled, stirred, and precipitated drop by drop with tannin (about 10 times the amount of titania) in fresh, strong solution. The red precipitate is treated as prescribed in § 49 ; the filtrate is boiled and tested by treatment with 0.5 g. of tannin and dropwise addition of 0.5*N* ammonia. If too little tannin has been added in the first

¹ *J. Chem. Soc.*, 1933, 423.

² Hillebrand and Lundell, *op. cit.*, p. 357.

precipitation, a further red precipitate will be produced without neutralisation, but normally only a small, dark vanadiferous precipitate is obtained : this collects any titania left in solution. This precipitate is collected and ignited together with the bulk.

The combined precipitates are re-treated as above, with 12 parts of tannin as precipitant. The precipitate, which is free from vanadium, is ignited, purified as usual, and weighed as TiO_2 ; the filtrate should be tested for complete precipitation.

The vanadium is determined in the combined, boiling filtrates by tannin and excess of ammonia (§ 78 (b)) ; the weighed precipitate should be tested for silica by bisulphate fusion and solution in dilute sulphuric acid. In accurate work the vanadium should be determined volumetrically (*cf.* § 78 (b)).

Two experiments (XXXII.) gave the following results :

G. taken.		Found.		Error.	
TiO_2 0.0724	V_2O_5 0.0407	0.0723	0.0402	- 0.0001	- 0.0005
„ 0.1039	„ 0.0434	0.1047	0.0431	+ 0.0008	- 0.0003

In the analysis of rutile I use the method here described for the determination of titania and the minute quantity of vanadic oxide usually present in the mineral, operating on 0.25g.

(d) *Micro-determination of Tantalum and Niobium.* See § 16.

6. PROCEDURES CARRIED OUT IN AMMONIACAL SOLUTION

We have to distinguish between procedures in which ammonia is added to mineral or acetic acid solutions, and others carried out in solutions of organic complexes not precipitated by ammonia alone.

§ 87. In mineral or acetic acid solutions, ammonia is the precipitating agent, and the addition of tannin with the ammonia precipitates the tannin adsorption complex instead of the hydroxide.

(a) *Alumina.* Divine's procedure (see § 72), facilitating the filtration of aluminium hydroxide, belongs to this category.

(b) *Beryllium.* Moser and Singer,¹ in describing the precipitation of beryllium by tannin and ammonia, point out that the method is specially suitable for minute amounts, on account of the bulkiness of the precipitate. This rule is of general applicability.

¹ *Monatsh. Chem.*, 1927, 48, 673.

Procedure. The weakly-acid solution (300-400 ml.), free from other metals except alkalis, is boiled with 20-30 g. of ammonium nitrate and treated with a 10 per cent. solution of tannin (10 times as much tannin as beryllia), followed by ammonia, drop by drop, until precipitation is complete. The bulky precipitate is collected and washed with hot water. If alkali salts are present, the precipitate is dissolved on the filter in a little hydrochloric acid; the solution is neutralised with ammonia and the precipitation repeated. The dried precipitate is ignited in platinum or silica, treated with a little nitric acid, dried, strongly ignited, and weighed as BeO.

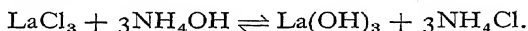
(c) *Rare Earths.* The solutions of salts of the rare earths are precipitated by ammonia, and this reaction is utilised for their quantitative determination, the precipitated hydroxides being ignited to oxides, or converted into oxalates. We have repeatedly observed that the recovery of the rare earths by ammonia precipitation is not always satisfactory, the filtrates from the hydroxide precipitates being liable to become cloudy on standing or cooling. The same observation is recorded in Rose's *Traité Complet de Chimie Analytique*.¹ Describing the precipitation of the ammonia group in the analysis of minerals containing rare earths, Rose recommends precipitation of the cold solution with excess of ammonia and filtration at ordinary temperature; the ammoniacal liquid containing the suspended precipitate should not be boiled or heated, because some yttria and ceria would dissolve.

In a private communication, Dr. Roger C. Wells has very courteously given me the following particulars, which explain the observed behaviour of the rare-earth group towards ammonia. To quote Dr. Wells, "the tendency of the rare earths to go into the filtrate, on precipitation with ammonia, has frequently been observed in the Survey Laboratory. Tests made by K. J. Murata and myself solved the difficulty. It appears that the stronger or more soluble bases among the rare earths, such as lanthana, require a decided excess of ammonia to coagulate and precipitate them completely. Merely making the solution alkaline to methyl red or even to phenolphthalein is quite ineffective. Enough ammonia should be added to cause malachite green to fade completely. We also found, as has been suggested before, that the presence of ammonium nitrate, or other similar salts, is harmful, requiring still more ammonia, and tending to dissolve the precipitate in any case. On boiling, the solution rapidly loses ammonia, thus increasing the solvent action, as may be easily shown with lanthanum. This behaviour seems to make boiling

¹ Vol. II, Paris, 1862, p. 460.

inadvisable, but warming assists coagulation of the precipitate. Evidently ammonium salts should be kept down in quantity by evaporating excess acid previous to precipitation with ammonia, and sufficient ammonia should be used both in precipitation and in wash-water."

In accordance with their strongly basic character, the rare earths are therefore capable of displacing ammonia from its salts, especially when the solution is heated; excess of ammonia and low concentration of ammonium salts favour the precipitation of the rare earths:



My collaborator, Mr. A. R. Powell, who confirms Dr. Wells's conclusions, has found that the addition of tannin with the ammonia used as precipitant for the rare earths facilitates their quantitative precipitation, the tannin precipitate showing no tendency to re-dissolve. Tannin is the most convenient reagent for testing the ammoniacal filtrate from a rare-earth precipitate obtained by ammonia.

§ 88. In Solutions of Organic Complexes not Precipitated by Ammonia Alone

In addition to the two tannin groups, A and B (§ 86 (a)), Schoeller and Webb (XXVII.) recognise a third group, C, the members of which (manganese, beryllium and the rare earths) are precipitated by tannin from ammoniacal tartrate solution; the precipitates are readily soluble upon acidification of the liquid which holds them in suspension.

(a) *Manganese* (XXVII.). The manganese-tannin complex is colourless, or nearly so; when freshly precipitated it is pale grey in appearance, but on exposure to air it darkens considerably; hence it turns brownish-black on the filter. The precipitation is practically quantitative. The hot tartrate solution is treated with ammonium chloride (10 g.) and acetate (5 g.), a fresh solution of 1 g. of tannin (for 0.05 g. of MnO), and a decided excess of ammonia. The liquid is allowed to stand overnight in the cold, and the precipitate is collected and washed with slightly ammoniacal 2 per cent. ammonium nitrate solution containing a little tannin. It is always contaminated with silica; hence it is ignited and dissolved in hydrochloric acid, the solution is evaporated to dryness, the residue is dissolved in dilute acid, and the manganese in the filtered solution is determined as pyrophosphate.

G. MnO taken.	MnO found.	Error.
0·0277	0·0272	— 0·0005
0·0484	0·0471	— 0·0013

The above procedure is not advocated as a method for the determination of manganese ; it is merely a contribution to the study of the action of tannin and the behaviour of metals in tartrate solution.

(b) *Beryllium*. Schoeller and Webb (XXX.) have effected the precipitation of beryllia from ammoniacal tartrate solution. The bisulphate melt of the oxide was dissolved in 100 ml. of 4 per cent. tartaric acid solution ; the liquid was treated with 30 ml. of strong hydrochloric acid and 5 g. of ammonium acetate, made ammoniacal, and diluted to 250 ml. The boiling solution, containing 2 ml. of free ammonia, was precipitated with a fresh solution of 0·5 g. of tannin (30 times the weight of BeO). The liquid was filtered after cooling ; the precipitate was washed with slightly ammoniacal ammonium chloride solution containing a little tannin, and ignited in a platinum crucible. The crude oxide was purified by fusion with sodium carbonate (§ 69).

G. BeO taken.	BeO found.	Error.
0·0110	0·0114	+ 0·0004
0·0080	0·0091	+ 0·0011
0·0133	0·0134	+ 0·0001
0·0141	0·0145	+ 0·0004

Generally speaking, tannin precipitations are more satisfactory in neutral, or faintly acid, than in ammoniacal solutions. Whilst the former yield light flocculent precipitates floating in a cloudless liquid, the latter (through co-precipitation of tannin) are apt to produce curdy or clotted precipitates and cloudy solutions which gradually darken by oxidation, with separation of a little black organic matter. Contamination of the tannin precipitates with silica from the glass vessels is more pronounced in ammoniacal solutions ; and for beryllium precipitations, we find it necessary to let the solution cool before collecting the precipitate, otherwise the filtrate may become cloudy and deposit a slight precipitate containing a minute quantity of beryllia.

(c) *Rare Earths*. The precipitation of the rare earths by tannin from ammoniacal tartrate solution was investigated by

Schoeller and Waterhouse (XXVIII.). The precipitates are colourless, excess of tannin causing a pale-brown discoloration, as in the case of alumina; the cerium precipitate, however, darkens considerably on exposure to air: it often turns almost black on the filter. The rare-earth complexes are readily soluble upon acidification with acetic acid of the liquid in which they are suspended.

For the quantitative investigation of the reaction, cerium and yttrium solutions of known content were diluted to 200 ml., boiled, and treated with the following reagents: 25 ml. of saturated ammonium chloride solution, 5 g. of sodium acetate, 0.5 g. of tannin in fresh solution, and ammonia until its smell became pronounced. In the tartrate tests, tartaric acid (4 g.) was added before the ammonia. The precipitates were allowed to settle on the water-bath, collected, well washed with ammonium nitrate solution, ignited strongly and weighed.

G. taken.	Solution.	Found.	Error.
CeO ₂ 0.0500	Acetate	0.0500	0.0000
„ 0.0500	Tartrate	0.0496	- 0.0004
Y ₂ O ₃ 0.0508	Acetate	0.0522	+ 0.0014
„ 0.0508	Tartrate	0.0508	0.0000

CHAPTER XV

QUALITATIVE ANALYSIS

Introduction

THE qualitative analysis of the earth acids and certain related elements involves the use of processes applied in quantitative analysis and explained in Parts I and II of this book. For this reason it has been found convenient to discuss the quantitative methods first.

The treatment of the qualitative analysis of tantalum and niobium in the text-books is quite inadequate and out of date. The subject had not been investigated since Marignac's time. Hence reactions of no diagnostic value, vague distinctions, and even faulty observations leading to erroneous conclusions, found their way into text-book after text-book; the unreliability of the information was surpassed only by that of the quantitative methods of earth-acid analysis.

Considerable advances in qualitative analysis have been made as a result of our researches. By applying the methods described in Chapters V to XII of this monograph, we are now able to detect and determine even subordinate quantities of any earth (with the exception of hafnia and the rarer members of the cerium and yttrium groups) in a complex mixture of any or all of them.

A scheme for the detection of all the earths must proceed along the lines of the quantitative separation procedure (Chapters VII to XII) because test-tube reactions for the identification of the pure compounds are unreliable in the presence of others. Hence the detection of the earths may require almost as much labour as their quantitative determination. If enough material is available, I would advise the operator to work on two weighed portions; the first or "pilot" portion is kept a step or two in advance of the other, the effect of the manipulations and the presence or absence of elements being noted. The proved absence of an element in the "pilot" simplifies the analysis of the other portion, the procedure for the separation and determination of that element being omitted.

The tests described in this chapter comprise the detection of tantalum and niobium in minerals (§ 89), the analysis of the tartaric hydrolysis precipitate (§ 90), the specific reactions of tantalum and niobium (§§ 91, 92), and the simultaneous identifica-

tion of tantalum and niobium (§ 93). A paragraph on the preparation of the pure pentoxides (§ 94) concludes the chapter.

§ 89. Joint Detection of Tantalum and Niobium in Minerals

(a) *By Tartaric Hydrolysis* (XV.). The finely-powdered mineral is fused with bisulphate, and the product is dissolved in hot tartaric acid solution (§ 8). The filtered liquid, boiled with one-fifth of its bulk of strong hydrochloric acid, furnishes a white flocculent precipitate of tantalic and niobic acids.

I consider tartaric hydrolysis the most important distinctive reaction for the joint detection of tantalum and niobium. The only other element precipitated under the above conditions is tungsten, but the precipitated tungstic acid is yellow. Tin is precipitated from tartrate solution by nitric, but not by hydrochloric acid, stannic chloride being soluble; besides, stannic oxide is almost insoluble in fused bisulphate, hence it cannot interfere in the above test.

Quantitative tests showing the sensitiveness of the reaction in presence or absence of titania are reproduced in § 53. These tests show a sensitiveness of the order of 0.03 mg. M_2O_5 per ml., the reaction being unaffected by five times that amount of titania. If a substantial amount of zirconia is present or suspected, it should be removed as in § 90 prior to the tartaric-hydrolysis test.

(b) *By Tannin*.¹ The tartaric-hydrolysis test described under (a) is conveniently carried out on quantities of 0.02 to 0.05 g. of mineral; the tannin reaction can be applied on a mg. scale.

The powdered mineral (2–3 mg.) is fused in a small silica crucible with a speck of bisulphate, and the melt is dissolved in 1 to 2 ml. of hot ammonium oxalate solution. The liquid is transferred to a very small test tube, treated at boiling heat with about 0.1 g. of ammonium chloride and 0.02 g. of solid tannin, and gently boiled for a short time. With minerals high in tantalum, a yellow precipitate is obtained; those containing more niobium give an orange to orange-red precipitate. Iron does not interfere in the slightly acid oxalate solution.

If the mineral contains titania—as proved by the hydrogen peroxide test in a separate portion—the test for earth acid must be modified as follows. The bisulphate melt of the mineral is extracted with 5 per cent. sulphuric acid containing 1 per cent. of tannin (pyrosulphate-tannin method, § 59); the orange to red residue is characteristic for the mixed pentoxides. For a confirmatory test, it is collected on a small pad of filter pulp, washed with dilute sulphuric acid, ignited in a small silica

¹ Schoeller, *Z. anal. Chem.*, 1934, 96, 252.

§ 89 TARTARIC-HYDROLYSIS PRECIPITATE

crucible, fused with bisulphate, and the oxalate solution of the melt is tested with tannin as described above.

The following results are reproduced from my paper :

Took 1 ml. of solution containing	Tannin reaction
0.3 mg. Ta_2O_5 .	Heavy yellow precipitate.
0.15 „ „ .	Immediate copious precipitate.
0.06 „ „ .	Immediate precipitate.
0.03 „ „ .	No distinct precipitate.
0.1 „ Nb_2O_5 .	Heavy red precipitate.
0.04 „ „ .	Orange precipitate.
0.02 „ „ .	Slight orange precipitate.

Hence the test permits the detection of 0.05 mg. Ta_2O_5 per ml., while the niobium reaction is about three times as sensitive. A euxenite (23 per cent. TiO_2 , 18 per cent. M_2O_5) was tested by the pyrosulphate-tannin method: 2.3 mg. was fused with bisulphate, and the melt extracted with hot acid tannin solution. This gave a flocculent red precipitate characteristic for niobium.

§ 90. Qualitative Analysis of the Precipitate Produced by Tartaric Hydrolysis

The precipitate must be tested for small amounts of tungstic acid, and co-precipitated titania and zirconia; the detection of tin—a very frequent minor associate of the earth acids—may conveniently be included in this set of operations.

The mineral, or oxide mixture, is fused with bisulphate, and the melt is dissolved in hot tartaric acid solution (§ 8). The unfiltered liquid is saturated with hydrogen sulphide, and the mixed precipitate and residue filtered off. It contains the whole of the tin (§ 22), which is detected in known manner after fusion of the ignited precipitate with cyanide, or reduction in a current of hydrogen or coal gas.

The tartaric-acid filtrate is boiled with one-fifth its bulk of strong hydrochloric acid, yielding the tartaric-hydrolysis precipitate. It has been observed that the earth acids precipitated by tartaric hydrolysis differ from each other in appearance: tantalic acid (or a precipitate composed mainly of this acid) is a sub-translucent, flocculent precipitate which settles readily, leaving the supernatant liquid clear; niobic acid is white and opaque, flocculates less readily and, after settling, leaves the liquid more or less milky. The precipitate is mixed with filter pulp, collected, washed with dilute hydrochloric acid, and ignited in a platinum crucible. It is then fused with potassium carbonate and the aqueous solution of the melt is boiled and treated with magnesia mixture (§ 38). The precipitate *MP* (*infra*), which contains the tantalum, niobium, titanium and zirconium, is filtered off, washed and ignited in a silica crucible.

The filtrate from *MP* contains the tungsten, which is recovered by the tannin-cinchonine method (§ 37). The ignited tannin-cinchonine precipitate, if substantially pure tungstic oxide, is deep-yellow to orange while hot, and soluble in hot, strong caustic soda. The filtered alkaline solution, upon acidification and treatment with cinchonine hydrochloride solution, yields a flocculent white precipitate; hydrochloric acid and zinc or stannous chloride produce a blue precipitate or coloration in the solution of sodium tungstate.

If the substance under investigation contains much niobium, the ignited tannin-cinchonine precipitate is usually white, not yellow. In this case it must be purified by fusion with sodium hydroxide, etc., as prescribed in § 39 (*b*). The ignited tannin-cinchonine precipitate obtained as a result of this re-treatment should be yellow and give the reactions just described; if not, then tungsten is absent.

Defacqz's test¹ is extremely sensitive, but unreliable when applied to impure tungstic oxide. It consists in the addition of solid phenol or hydroquinone to the cold solution obtained by fusing the oxide with a little bisulphate and adding enough strong sulphuric acid to prevent solidification on cooling. Tungsten gives intense colorations (reddish-brown with phenol and violet with hydroquinone). But apart from the known fact that titania reacts just as strongly, we found that niobium, which follows tungsten most tenaciously, also gives vivid colour reactions (orange-yellow and deep reddish-brown, respectively (XXXI)).

The precipitate *MP*, having been ignited in a silica crucible, is fused with bisulphate, and the melt is subjected to the pyrosulphate-tannin method, *i.e.*, extraction with acidified tannin solution (§ 59). The brightly-coloured residue, consisting of the tannin complexes of the earth acids, is filtered off, and the filtrate collected in a conical flask.

Identification of Tantalum and Niobium. The precipitated tannin complexes have a buff to bright scarlet colour, according to the composition of the oxide mixture. The precipitate is quite different from the flocculent, voluminous tannin complexes obtained by precipitation: it is remarkably compact, and partly retains the shape of the fragments of the melt if the mixed oxides contain much earth acid. For the separate identification of tantalum and niobium, the precipitate is treated as in § 93 (*b*).

Identification of Titanium and Zirconium. The filtrate from the earth-acid complexes is rapidly boiled down in the conical flask with 5 ml. of strong sulphuric acid until it darkens and foams.

¹ *Compt. rend.*, 1896, 123, 308.

It is then treated with small portions of strong nitric acid till it becomes clear and colourless. The liquid is then heated over a bare flame until copious white fumes are given off, a few more drops of nitric acid being added, if necessary, to bring about complete decolorisation. After cooling, 50 ml. of cold water are added, followed by hydrogen peroxide; the familiar yellow to orange colour proves the presence of titania. Zirconia is next detected by addition of excess of ammonium phosphate, which precipitates flocculent colourless zirconium phosphate.

§ 91. Specific Tantalum Reactions

(a) The tantalum reaction *par excellence* is the formation of the sulphur-yellow tannin precipitate in weakly-acid oxalate solution containing ammonium chloride. Most of the text-books state that the tantalum-tannin precipitate is light brown (or yellow-brown), but it cannot be emphasised too strongly that this is not the case. A tantalum solution that gives a light-brown tannin precipitate contains titanium (see § 93).

The bisulphate melt of the mineral, oxide or other compound is dissolved in saturated ammonium oxalate solution, and the boiling liquid is treated with tannin solution until a yellow coloration is obtained. Addition of saturated ammonium chloride and further boiling produce the yellow flocculent precipitate; if the solution is rather acid, cautious addition of a few drops of dilute ammonia will expedite the formation of the precipitate.

If an orange to red tannin precipitate is obtained, the solution contains probably more niobium than tantalum, and further manipulation is required for the detection of tantalum (§ 93).

(b) Tantallic oxide dissolves completely in molten potassium carbonate. The melt dissolves in water, and the solution, when saturated with solid sodium chloride, gives a pulverulent white precipitate of sodium tantalate; when acidified with hydrochloric acid, it gives a flocculent precipitate of tantallic acid which turns pale yellow on treatment with tannin solution.

(c) Tantallic acid is soluble in hydrofluoric acid, and the concentrated solution gives with potassium fluoride a crystalline precipitate consisting of rhombic needles, K_2TaF_7 . The reaction is not very sensitive as the precipitate is soluble in about 200 parts of water.

(d) Zinc dust and phosphoric acid produce no coloration in tantalum solutions (*cf.* Niobium, § 92 (f)).

(e) The precipitation of the oxyfluoride $K_4Ta_2O_5F_{14}$ has been advanced as the most sensitive test for small quantities of tantalum. The above formula is assigned to the white insoluble powder

produced by boiling a solution of potassium fluorotantalate. Krüss and Nilsson¹ proved that potassium oxyfluoroniobate free from tantalum gives a similar insoluble compound when its solution is boiled. In our own experience (V.), if an insoluble white powder is obtained when the mixed complex fluorides are boiled with water, some niobium is found in the precipitate, and a good deal of tantalum in the filtrate, even after the salt mixture has been kept at 170° C. for several hours; further, the tantalum is not completely removed from the niobium fraction after several repetitions of the procedure, contrary to Hall's statement.² The reaction must be rejected as unreliable.

§ 92. Specific Niobium Reactions

(a) The formation of the scarlet-red niobium-tannin adsorption complex is not altogether specific for niobium, as the precipitate is practically indistinguishable from the titanium-tannin complex. The precipitates of niobium and titanium are obtained under the same conditions as the tantalum complex (§ 91 (a)). In the reactions enumerated below, the behaviour of titanium under the same conditions is indicated.

(b) Niobic oxide is easily soluble in molten potassium carbonate. The aqueous solution of the melt, when saturated with solid sodium chloride, yields a rather coarse crystalline precipitate of sodium niobate; with excess of hydrochloric acid it gives a white precipitate of niobic acid which turns orange on treatment with tannin solution. Titania is not dissolved by molten potassium carbonate.

(c) Niobic acid is precipitated from the boiling tartrate solution by strong hydrochloric acid (tartaric hydrolysis). Titanium solutions give no precipitate under the same conditions.

(d) When niobic oxide is fused with bisulphate and the melt treated with a mixture of dilute sulphuric acid and hydrogen peroxide, a colourless solution is obtained. Titania under the same conditions gives a deeply-coloured, yellow to orange solution.

(e) Niobic acid is soluble in hydrofluoric acid; the solution is not precipitated by potassium fluoride under the conditions of the tantalum test (§ 91 (c)).

(f) The solution of potassium niobate, obtained as under (b), is acidified with phosphoric acid and concentrated by evaporation until the precipitate has re-dissolved and the liquid is syrupy. This is diluted with about twice its volume of water and boiled with 1 g. of zinc dust: the solution turns black, brown

¹ *Ber.*, 1887, 20, 1676.

² *J. Amer. Chem. Soc.*, 1904, 26, 1239.

or yellow, according to the quantity of niobium present.¹ Tantalum does not react under these conditions. Titanium in phosphoric acid gives violet or lilac colorations when reduced with zinc dust in presence of sufficient phosphoric acid.

§ 93. Simultaneous Identification of Tantalum and Niobium

The operator should always aim at obtaining the mixed earth acids in the form of a tartaric hydrolysis precipitate (§§ 89 (a), 90). The formation of this precipitate proves the presence of the earth acids ; the procedure given below serves for their separate identification.

The tartaric hydrolysis precipitate is well washed and ignited. A small portion is then tested for titania by fusion with bisulphate and solution of the melt in acidified hydrogen peroxide (§ 92 (d)). Freedom of the precipitate from appreciable amounts of titania is of great importance in the detection of small quantities of tantalum. We will therefore consider two cases in the identification procedure :

(a) *The Tartaric Hydrolysis Precipitate is practically free from Titania.* The bulk of the precipitate is fused with bisulphate, and the cold mass is dissolved in hot ammonium oxalate solution. The boiling liquid is treated with 0.2 to 0.3 g. of tannin, 5 g. of ammonium chloride, and 0.5*N* ammonia, if necessary, drop by drop, till a flocculent precipitate is formed. If the precipitate is pale yellow to bright yellow, the presence of tantalum is proved. If however the precipitate is orange to red, niobium is present, whilst tantalum is either absent or present in subordinate amount. In such a case the precipitate is collected, washed with ammonium chloride solution, ignited, and fused with bisulphate. The melt is again dissolved in ammonium oxalate solution, and the liquid is treated with 0.1 to 0.2 g. of tannin, and ammonium chloride and ammonia as before until a flocculent precipitate is again obtained. This will now be yellow if the amount of tantalum is not too small ; if again orange, it should be collected and the treatment repeated once more. For the detection of traces of tantalum, it is necessary to proceed as in § 63.

In presence of much tantalum, niobium is readily detected in the filtrate from the yellow tantalum precipitate : the boiling liquid is treated with more tannin and a fair excess of sodium or ammonium acetate, which precipitates the vermilion niobium-tannin complex. If tantalum is still present in appreciable amount, a mixed precipitate of orange to orange-red colour will be obtained.

¹ Giles, *Chem. News*, 1907, 95, 1.

(b) *The Tartaric Hydrolysis Precipitate contains Titania.* The bulk of the precipitate is fused with bisulphate, and the cold mass is extracted with a 1 per cent. solution of tannin in 5 per cent. sulphuric acid, as described in § 59. The coloured residue is collected, well washed with 2 per cent. sulphuric acid, ignited, and fused with bisulphate.

With tartaric hydrolysis precipitates rich in titania, it is advisable to test for the completeness of its removal by the above process, by detaching a fragment of the bisulphate melt and testing it with acidified hydrogen peroxide. If a fairly strong yellow coloration is thus obtained, the extraction of the bisulphate melt with acid tannin solution should be repeated. The coloured residue from the second extraction is again collected, washed, ignited, and fused with bisulphate.

The bisulphate melt from the single or double treatment is dissolved in hot ammonium oxalate solution, and the solution is tested for tantalum and niobium as under (a) above.

§ 94. Preparation of Pure Tantalum and Niobic Oxides

The analyst who intends to specialise in earth-acid analysis is advised to prepare his own stock of pentoxides for use in investigational work, and to test the purity of his preparations by means of the methods given in this book.

The most convenient decomposition method for earth-acid minerals is that of W. B. Giles.¹ The finely-powdered mineral (high-grade tantalite or columbite) is mixed with 3 parts of potassium carbonate and transferred to a steel crucible provided with a well-fitting cover which overhangs the edge of the crucible. A crucible $2\frac{1}{2}$ inches high, $2\frac{1}{2}$ inches across the top and $1\frac{3}{8}$ inches across the bottom will take 25 g. of ore and the necessary flux. The covered crucible is placed in a fireclay or graphite crucible and the space between the two is filled with coarsely powdered charcoal nearly to the top of the steel crucible. The remaining space is filled with broken charcoal about nut size, and the outer crucible is closed with a well-fitting lid.

The crucible is slowly heated in a coke or gas furnace, being kept at moderate red heat for an hour, during which carbon dioxide escapes through the porous mass. The heat is then raised to the highest temperature of the furnace, which is maintained for another hour.

Under the reducing conditions realised by the procedure, the stannic oxide in the mineral is reduced to metal, which plates the interior of the steel crucible. The iron is mostly reduced to metal,

¹ *Chem. News*, 1909, 99, 1.

while manganous oxide and other impurities including titania form a heavy layer of black, sandy powder.

When the cold crucible is opened, the contents usually come out in one piece. The crucible can be used for a number of fusions. The melt is broken up in a mortar and stirred in a tall beaker with 500 ml. of hot water until disintegrated. After standing for an hour, the clear or nearly clear supernatant liquid is syphoned off and freed from suspended matter by suction filtration through a deep layer of filter pulp.

Giles decomposes the potassium salts at this stage by pouring the solution into dilute hydrochloric acid, but I recommend precipitation of the earth acids as sodium salts, so as to eliminate the small amounts of tungstic and silicic acids present. The filtered solution contained in a 2-litre beaker is stirred and treated with strong caustic soda until precipitation is complete. The white crystalline precipitate is left to settle, the mother-liquor is decanted off, and the precipitate is washed repeatedly by decantation with 10 per cent. caustic soda.

The precipitate is treated with a litre of boiling-hot distilled water; the suspension is well stirred and treated with dilute hydrochloric acid in moderate excess. The beaker is allowed to stand on a hot plate for an hour with frequent stirring; the hot liquid is then made ammoniacal, removed from the hot plate, and left to itself until quite clear, when it is syphoned off. The white flocculent precipitate of earth acids is washed several times with 500-ml. portions of 1 per cent. ammonium chloride solution; it is then collected, washed, dried, and ignited in porcelain crucibles.

The ignited pentoxides are ground wet in a porcelain mortar and boiled several times with 2 per cent. hydrochloric acid, which is made ammoniacal and decanted through a filter; they are finally collected, washed with dilute ammonium nitrate solution, and strongly ignited in porcelain crucibles.

The purified mixed oxides thus obtained should be sufficiently pure to be used for analytical purposes after having been tested and analysed.

Combined water (loss on ignition test) and *soda* (flame test) are eliminated by repeated lixiviation and strong ignition.

Silica, iron and sulphide-forming metals; 0.25 g. of pentoxide is fused with 3-4 g. of pure, silica-free potassium bisulphate (§ 13), the melt is dissolved in tartaric acid (§ 8), and the solution is filtered through a small filter, which is washed with hot water and ignited. The residue, if any, is weighed and treated in a small tared platinum cup with hydrofluoric and sulphuric acids, silica being determined by difference.

The tartaric acid filtrate is treated hot with 10 ml. of 5 per cent. sulphuric acid and a stream of hydrogen sulphide ; no coloration or precipitate should appear after 15 minutes' treatment. The liquid is then made ammoniacal and left overnight (test for iron).

Titanium is determined colorimetrically in 0.1 to 0.2 g. of oxide, after bisulphate fusion and solution in ammonium oxalate (§ 58).

Determination of Tantalum and Niobium Oxides. 0.25 g. is analysed according to § 61.

In the great majority of cases, test and practice analyses may be conducted with the mixed pentoxides, especially if two preparations are available, *viz.*, a pentoxide rich in tantalum, prepared from tantalite (sp. gr. 7+) and another rich in niobium, prepared from columbite (sp. gr. 5.5).

To prepare pure tantalum oxide, high-grade tantalite is treated by Giles's process (*supra*) ; the unignited precipitate obtained by decomposition of the sodium salt is dissolved in hydrofluoric acid, and the solution is treated with potassium fluoride (§ 64) ; the first crop of crystals is collected (rubber funnel) and recrystallised from hot water acidified with hydrofluoric acid.

The recrystallised salt is heated with excess of strong sulphuric acid in a platinum dish until all the hydrofluoric acid has been expelled. The acid mass is transferred to a large beaker, diluted with hot water, the liquid is made ammoniacal and digested on a hot plate for some time. After the precipitate has settled, the clear liquor is syphoned off and the precipitate is repeatedly washed by decantation with ammonium nitrate solution. The precipitate is finally collected, dried, ignited and lixiviated, etc., like the mixed pentoxides.

Smaller quantities of tantalum oxide may be prepared by the tannin method ; this applies also to niobium oxide, for the purification of which no other small-scale process is available.

For the preparation of pure tantalum oxide, four 0.25-g. portions are separately fused with bisulphate and the fusions are dissolved in ammonium oxalate solution. The boiling solutions are precipitated without previous neutralisation with about 1 g. of tannin and 5 g. of ammonium chloride per portion. The yellow precipitates are combined in a large beaker, left to settle, washed several times by decantation with ammonium chloride solution, and collected in a Büchner funnel. After having been dried, the precipitate is ignited, leached, and again ignited.

Pure niobium oxide is prepared from a niobium-rich pentoxide preparation in a similar manner. In this case, one or several 1-g. portions can be worked up. Each portion is fused with 6 g.

of bisulphate, the melt is dissolved in 150 ml. of ammonium oxalate solution, and the hot liquor (500 ml.) is neutralised with dilute ammonia until the precipitate re-dissolves slowly. It is then boiled, stirred and treated gradually with 0.2 to 0.4 g. of tannin (depending on the tantalum present), followed by 5 g. of ammonium chloride. After an hour's digestion on a hot plate, the precipitate is filtered off by suction; the filtrate is boiled and treated with 0.2 g. of tannin as before. The precipitate thus obtained should be bright red without any orange tinge, as a proof that practically all of the tantalum has been eliminated in the first fraction. After standing hot for some hours, the liquid is left overnight in the cold. It is syphoned off, filtered into a large beaker, boiled, and precipitated with 4 to 5 g. of tannin and 10 g. each of ammonium chloride and acetate.

The niobium precipitate is left to settle; the supernatant liquid is drawn off and the precipitate is repeatedly washed by decantation. It is then collected in a Büchner funnel, ignited, lixiviated, etc., as for the tantalum precipitate.

Needless to say, both preparations should be tested for purity (see § 63 for niobic oxide, and § 64 for tantalic oxide).

CHAPTER XVI

THE LITERATURE ON EARTH-ACID ANALYSIS

THIS chapter is not intended to present a bibliography on the subject of earth-acid analysis. Such a compilation would serve no useful purpose in a laboratory manual because the record of the earlier work, whilst of historic and scientific interest, is almost wholly one of failure and therefore of no practical use to the analyst.

I may point out that, of the separation methods involving tantalum and niobium and published prior to 1919 (the year in which we began our investigations), only three have survived in this monograph. They are: (1) the separation of iron from the earth acids by Berzelius's method, *i.e.*, by precipitation of ferrous sulphide from ammoniacal tartrate solution (§ 26); (2) J. L. Smith's hydrofluoric-acid method for the separation of the rare earths from the earth acids (§ 30); and (3) Bedford's procedure for the separation of tungsten from niobium, embodied in our magnesia method for the separation of tungstic acid from the earth acids and other earths (§ 38).

The reader interested in earth-acid analysis as we found it about twenty years ago is invited to consult the only other monograph on the subject, published in 1912 by R. J. Meyer and O. Hauser (chapters on titanium, zirconium, thorium, niobium and tantalum by Hauser), and referred to in Chapter I. By comparing the chapters in question with the present volume, he will convince himself that the technique of earth-acid analysis has changed out of all recognition.

With the practical experience acquired during seventeen years' continuous and painstaking research work, I have to say, without feeling guilty of boastful exaggeration, that our *Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates* mark an entirely new departure in this province of mineral analysis.

This monograph is a systematic presentation of the subject of the *Investigations* which occupy close on 200 pages of print. In re-arranging the text-matter of our papers into a compact manual for more general laboratory use, I have been as economical of space as possible. Those desiring still further information should consult the original papers, where additional experiments

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and other details may be found on a number of subjects, including the re-investigation of older methods. In order to facilitate the search amongst our papers I have compiled the following list, in which they are first classified under seven heads, then given in chronological order, with titles and summaries fully reproduced.

CLASSIFIED LIST OF PAPERS

(The Arabic numerals correspond to the sectional numbers in Roman numerals.)

1. *Analytical technique* : 6, 12, 19.
2. *Tartaric-acid method* : 1, 10, 16, 17, 20, 22, 27, 33.
3. *Separation of tungsten from the earth acids and other earths* : 7, 8, 26, 29, 31.
4. *Separation of tannin group A from group B* : 2, 13, 18, 23, 25.
5. *Separation of titania from the earth acids* : 9, 14, 15, 21.
6. *Separation of tantalum from niobium* : 3, 4, 5, 11, 24.
7. *Other associated elements* : 27, 28, 30, 32.

CHRONOLOGICAL ORDER OF PAPERS

I. *The Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates*. (Schoeller and Powell, *J. Chem. Soc.*, 1921, 120, 1927 ; abstr. *Analyst*, 1922, 47, 93.)—The usual procedure for the analysis of tantalum-columbium minerals is briefly discussed. A new method of analysis is outlined, in which the initial hydrolysis is avoided by solution of the pyrosulphate melt in tartaric acid solution.

II. *The Separation of Zirconium from Tantalum and from Columbium*. (Schoeller and Powell, *J. Chem. Soc.*, 1921, 120, 1931 ; abstr. *Analyst*, 1922, 47, 93.)—The separation of zirconia from columbium pentoxide by fusion with potassium carbonate is quantitative within the limits of experimental error. It is advisable to submit the fusion residue to a second fusion.

The separation of zirconia from tantalum pentoxide by fusion with potassium carbonate is less satisfactory than the preceding. Even after three fusions, the results show a positive error of 2 to 8 mg. for zirconia, and a corresponding negative error for tantalum pentoxide. Roughly speaking, 80 to 90 per cent. of the tantalic acid present is rendered soluble in the first fusion.

The fusion method described in this section should prove more especially useful for estimating zirconia in columbate minerals poor in tantalum. It may also be applied in the analysis of tantalocolumbates for checking the purity of zirconia pre-

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cipitates, or ascertaining the presence of small quantities of zirconia in precipitates obtained by the usual method of hydrolysis.

III. *The Volumetric Estimation of Columbium.* (Schoeller and Waterhouse, *Analyst*, 1924, 49, 215.)—Theoretical considerations and the results of original tests are submitted to prove that the existing methods for the volumetric estimation of columbium are unreliable. These methods furnish empirical factors. The view is advanced that the criterion of an accurate volumetric method should be a stoichiometric factor, indicating reduction to a definite oxide.

IV. *A New Method for the Separation of Tantalum from Niobium.* (Powell and Schoeller, *Analyst*, 1925, 50, 485.)—A new method for the separation of tantalum from niobium is described. It is based upon differential hydrolytic dissociation between oxalotantalic and oxaloniobic acids in presence of tannin in slightly acid solution. The method possesses the following advantages. The colour of the tantalum precipitate indicates at a glance whether it is free from, or contaminated with, niobium; no platinum vessels are required; and the accuracy approximates to that reached in the separation of most of the common elements.

V. *The Detection and Determination of Tantalum in Niobium Compounds.* (Powell and Schoeller, *Analyst*, 1925, 50, 494.)—The inadequacy of the usual qualitative tests for tantalum is discussed. The tannin method for the separation of tantalum from niobium is shown to be applicable to the detection as well as the determination of small quantities of tantalum in niobium compounds, and to the certain identification of the two elements in admixture by the production of precipitates of characteristic colour.

VI. *The Precipitation of the Earth Acids by Sodium Compounds.* (Schoeller and Jahn, *Analyst*, 1926, 51, 613.)—When tantalic oxide is fused with potassium carbonate and the solution of the mass treated with sodium chloride, 4 : 3 sodium tantalate is precipitated. Niobic oxide treated in the same manner yields 7 : 6 sodium niobate. The precipitates are dense, micro-crystalline powders. The filtrates contain a few mg. of non-precipitated earth acid, substantial recovery of which is effected by partial neutralisation to the bicarbonate stage and digestion on the water-bath: hydrolytic dissociation in alkaline solution takes place, and the earth acid is precipitated. Sodium tantalate and niobate are decomposed by dilute acid; the quantity of the latter is proportional to that of the alkali in the precipitates. This reaction was applied to the indirect volumetric determination of the earth

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acids in the mixed sodium salts, but the results were rather wide as the end-point could not be ascertained with sufficient sharpness by the use of colour indicators. The analytical applications of the precipitates are under investigation.

VII. *The Precipitation of Tungstic Acid by Tannin.* (Schoeller and Jahn, *Analyst*, 1927, 52, 504.)—A method is described for the precipitation of small quantities of tungstic acid from solutions containing alkali chloride. The acidified solution is boiled with tannin and complete flocculation of the brown tungsten precipitate is accomplished by addition of cinchonine hydrochloride; the precipitate is ignited to tungsten trioxide. The results are accurate.

VIII. *The Separation of Tungsten from Tantalum and Niobium.* (Schoeller and Jahn, *Analyst*, 1927, 52, 506.)—The following methods for the separation of tungsten from tantalum and niobium are shown to be unreliable: (1) extraction of the precipitate, obtained by hydrolysis after bisulphate fusion, by ammonium sulphide or hydroxide (Berzelius); (2) precipitation of the solution of the potassium salts by boiling with ammonium nitrate; and (3) fusion of the mixed oxides with sodium carbonate and sulphur (Rose).

The authors' separation methods are based on the precipitation of sodium tantalate and niobate. The separation of small quantities of tungsten from considerable amounts of the earth acids is effected by fusion of the mixed oxides with potassium carbonate, precipitation of the resulting solution with sodium chloride, recovery of the small quantity of non-precipitated earth acid by hydrolysis in bicarbonate solution, and precipitation of the tungstic acid in the filtrate by tannin and cinchonine. For the determination of small quantities of earth acid in tungsten trioxide, the latter is fused with sodium hydroxide and the fused mass dissolved in sodium chloride solution; sodium tantalate and niobate remain undissolved. The two methods give satisfactory results.

IX. *The Separation of Titanium from Tantalum and Niobium.* (Schoeller and Deering, *Analyst*, 1927, 52, 625.)—The recent literature on the separation of titania from the earth acids is reviewed and criticised, to which end several processes were re-investigated. The following conclusions have been reached: (1) Hauser's mannitol method, which was apparently abandoned by its originator, is shown not to effect a separation. (2) The methods proposed by Weiss and Landecker were tested and criticised by a number of investigators, none of whom could reproduce a reliable separation. (3) Muller's potassium carbo-

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nate and salicylic acid process is relatively the best of the published methods. The very favourable results reported by him could not, however, be obtained; the earth-acid fractions obtained by the authors, although still titaniferous, gave consistently low recoveries. (4) Neither salicylic acid nor ammonium salicylate extracts titania from a pyrosulphate-hydrolysis precipitate, but titanic acid precipitated by ammonia is soluble in either reagent; in the case of mixed earth-acid and titania precipitates produced by ammonia, a more or less considerable proportion of the titania content is rendered soluble, but no quantitative separation is achieved. (5) Fusion of the mixed oxides with potassium carbonate and extraction of the mass with water is quite ineffective as a means of separation. (6) Volumetric methods for the simultaneous oxidimetric determination of titanium and niobium in presence of tantalum are too uncertain to serve as a substitute for actual separation.

A preliminary notice is given of the authors' proposed separation method, based on the dissociation of the soluble tartaric complexes of the metallic acids by a mineral acid; the earth acids are precipitated, the titanic salt remains in solution. The results obtained are, as yet, only approximate; further work aiming at an exact separation is now in progress.

X. *The Separation of Silica from the Earth Acids.* (Schoeller and Powell, *Analyst*, 1928, 53, 258.)—The disputed volatilisation of the fluorides of tantalum and niobium is discussed. Evaporation of the mixed oxides with hydrofluoric and sulphuric acids, whilst suitable for determining small amounts of earth acid in silica, is neither convenient nor accurate for the determination of a small amount of silica in earth acids. In the latter case, fusion of the mixed oxides with sodium hydroxide and treatment of the mass with water, as well as fusion with potassium carbonate, followed by precipitation with sodium chloride, gives low silica recoveries; accurate results are, however, obtained by fusion of the mixed oxides with bisulphate, extraction of the melt with oxalic or tartaric acid, and treatment of the impure silica residue with hydrofluoric and sulphuric acids.

In a discussion on the relative merits of potassium carbonate and bisulphate for the decomposition of earth-acid minerals, preference is given to the bisulphate chiefly because the silica is not converted into soluble silicate, as is the case in the carbonate fusion; hence it is unnecessary to submit the main earth-acid fraction to hydrofluoric acid treatment.

XI. *The Precipitation of Titanium by Tannin.* (Schoeller and Powell, *Analyst*, 1928, 53, 264.)—Tannin produces a red precipi-

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tate in oxalic or tartaric solutions of titanium ; the precipitation is quantitative in the neutralised solution. Titania interferes with the tannin separation of tantalum from niobium, if present in quantities higher than about one-hundredth of the tantalic oxide, by causing a discoloration of the yellow tantalum precipitate.

XII. *Observations on the Pyrosulphate-Hydrolysis Method.* (Schoeller and Waterhouse, *Analyst*, 1928, 53, 467.)—The pyrosulphate-hydrolysis method has been experimentally investigated, with the following results : (1) The procedure does not afford a quantitative separation of the earth acids from zirconia by any of the modifications tried ; a decrease in the quantity of co-precipitated zirconia is achieved at the cost of slightly incomplete earth-acid precipitation. (2) The department of mixtures of earth acid and titania is such that no separation of any practical significance takes place at any stage preceding total precipitation. (3) Zirconia prevents the hydrolytic precipitation of titania, and of the earth acids as well when titania is also present. (4) The separation of the earth acids from ferric sulphate is not feasible ; the separation from ferrous sulphate is very much better, but not perfect. (5) The conclusion reached is, that the procedure is not a separation process ; it is a very indifferent precipitation method, subject to the above and other causes of error. It should fall into disuse as the field of earth-acid analysis becomes more thoroughly explored.

XIII. *A New Method for the Separation of Zirconium and Hafnium from Tantalum and Niobium.* (Schoeller and Waterhouse, *Analyst*, 1928, 53, 515.)—A new method is described for the separation of small quantities of earth acids from large amounts of zirconia (hafnia). The process is based on the precipitation of the oxalo-earth acids by tannin in weakly-acid solution, zirconyl oxalate remaining dissolved. The method described in an earlier Section [II]—fusion of the mixed oxides with potassium carbonate—has been perfected, with the result that a single fusion may be sufficient for the separation of the bulk of the earth acids. The balance is then separated from the zirconia residue by the tannin procedure. This is a delicate test for the detection of the smallest quantities of earth acids in zirconia.

XIV. *A new Method for the Separation of small Quantities of Tantalum and Niobium from Titanium.* (Schoeller and Jahn, *Analyst*, 1929, 54, 320.)—A new method is described for the separation of small quantities of earth acids from large amounts of titania. The solution, containing the oxalates of titanium and ammonium and the oxalo-earth acids, is treated with sodium salicylate, whereby the titania becomes converted into a stable

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crystalloidal sodium titanylsalicylate. The hot solution is then precipitated with calcium chloride, the bulky precipitate carrying down the earth acids. They are recovered by solution of the precipitate in hydrochloric acid, destruction of the oxalic acid with permanganate, and precipitation with tannin. The tannin precipitate is purified by fusion with bisulphate, solution in tartaric acid, and boiling with excess of nitric acid in very small bulk. The soluble titania fraction is again submitted to the above procedure, after having been precipitated by evaporation and saturation with ammonium chloride of the filtrate from the oxalate precipitate. The errors are consistently negative, a few mg. of earth acid escaping precipitation ; but serviceable results are secured by the application of an empirical correction. The final pentoxide precipitate is free, or practically free, from titania.

XV. *A new Method for the Separation of Tantalum and Niobium from Titanium and Zirconium (1 : 1. Qualitative).* (Schoeller, *Analyst*, 1929, 54, 453.)—A new process (the "pyrosulphate and tannin method") is described for the qualitative separation of tantalum and niobium from titanium and zirconium. It consists in fusing the mixed oxides with bisulphate and extracting the fusion product with 5 per cent. sulphuric acid containing 1 per cent. of tannin. The earth acids remain insoluble as coloured tannin adsorption complexes, whilst the sulphates of titanium and zirconium dissolve. The addition of the tannin prevents the formation of complexes, which render the separation ineffective when the bisulphate melt is leached with cold water or dilute acid.

The most reliable tests for tantalum and niobium are discussed : it is shown that the precipitation of the earth acids from boiling tartrate solutions by excess of mineral acid is a specific, sensitive and convenient earth-acid reaction applicable in presence of other metals. A preliminary notice is given of the quantitative application of the pyrosulphate and tannin method. The salicylate process for the separation of titanium from tantalum, niobium and zirconium is adversely criticised.

XVI. *Observations on Tartaric Hydrolysis.* (Schoeller and Webb, *Analyst*, 1929, 54, 704.)—Precipitation of the earth acids from tartrate solution by mineral acid, previously shown to be a sensitive and specific earth-acid reaction, has now been investigated as a quantitative method. Precipitation of tantalic and niobic, also tungstic, acids is never quite quantitative ; a few mg. escape precipitation. Of all the other mineral associates of the earth acids, only titanium and zirconium interfere to a certain extent with the normal course of the reaction. Means for

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obviating this interference will be studied ; the recovery of the small fraction of non-precipitated earth acid from the tartrate solution will be discussed in the next section.

XVII. *The Quantitative Precipitation of the Earth Acids and certain other Oxides from Tartrate Solution.* (Schoeller and Webb, *Analyst*, 1929, 54, 709.)—The earth acids are quantitatively precipitated from tartrate solution by tannin after neutralisation or addition of excess of ammonium acetate ; we utilise this reaction for the recovery of the earth acid fraction not precipitated by tartaric hydrolysis. Zirconia and titania are likewise precipitated, but accurate neutralisation after addition of the tannin is required. Thoria and alumina are precipitated like the earth acids. The reaction is useful and convenient for the direct determination of small quantities of alumina after precipitation of iron as sulphide. Cupferron is available for the quantitative recovery of the earth acids from tartrate solutions in presence of mineral acid. The earth acids and their mineral associates are classed into analytical groups according to their precipitability from tartrate solution.

XVIII. *A new Method for the Separation of Titanium from Zirconium and Hafnium.* (Powell and Schoeller, *Analyst*, 1930, 55, 605.)—The present position of the titania-zirconia separation is reviewed, Dittrich and Freund's salicylate method being re-investigated. In our hands, the process did not lead to a clean-cut separation, the zirconia residue from a double treatment still containing titania, while some zirconia accompanied the titania into the filtrates. A new method is explained, based upon precipitation of the titania by tannin from a neutralised oxalate solution half-saturated with ammonium chloride ; a repetition of the procedure results in the quantitative precipitation of the titania with only traces of zirconia, if any. The method is simpler and quicker than the published processes. A preliminary account is given of the extension of the new method to the separation of the earth acids or titania or both from any or all of the following : zirconia, thoria and alumina.

XIX. *Laboratory Notes on Analytical Technique.* (Schoeller, *Analyst*, 1931, 56, 304.)—The following manipulations of fundamental importance in earth-acid analysis are discussed and described : bisulphate fusion, solution of the melt in oxalate or tartrate solution ; tannin precipitation of the earth acids from tartrate and from oxalate solution ; filtration, washing, ignition and purification of precipitates ; a micro-test for earth acids.

XX. *The Separation of Tin from Tantalum and Niobium.* (Schoeller and Webb, *Analyst*, 1931, 56, 795.)—The following

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two cases are considered: (1) Separation of small amounts of tin from much earth acid. Simpson's process (fusion with potassium hydroxide and precipitation of the earth acids with hydrochloric acid) was found to give slightly low results for both tin and earth acid. Giles's process (fusion with potassium carbonate, solution in citric acid, and precipitation of tin as sulphide) is criticised, being shown not to be suitable for earth-acid minerals. Schoeller and Powell's method (fusion with bisulphate, solution in tartaric acid, treatment with hydrogen sulphide, collection of insoluble residue and sulphide precipitate) was investigated and found to be serviceable. (2) Separation of small amounts of earth acid from much tin. The separation is based on the reduction of the tin oxide by hydrogen. Finally, the separation of earth acid, tin oxide and silica is discussed.

XXI. *A Reliable Method for the Quantitative Separation of Titanium from Tantalum and Niobium.* (Schoeller and Jahn, *Analyst*, 1932, 57, 72.)—The oxalate-salicylate method for the separation of titania from the earth acids, described in an earlier paper [XIV.], has now been perfected, with the result that an almost quantitative recovery of the earth acids is achieved, and that less than 1 mg. of titania remains in the final pentoxides. The process is claimed to be accurate within 0.5 per cent. The application of the pyrosulphate tannin method to the determination of small amounts of earth acid in titania is explained. The principles underlying the separation of titania from the earth acids are briefly discussed.

XXII. *The Separation of the Earth Acids from Metals of the Hydrogen Sulphide Group.* (Waterhouse and Schoeller, *Analyst*, 1932, 57, 284.)—The separation of tantalum and niobium from antimony, bismuth and copper was studied. When the mixed oxides are fused with bisulphate, the mass dissolved in tartaric acid, and the clear solution treated with hydrogen sulphide, the sulphide precipitate was always found to be contaminated with a few mg. of earth acid. The co-precipitation is ascribed to hydrolytic decomposition of the tartaric earth-acid complexes. The separation is completed by further treatment of the sulphide precipitate; this is dissolved in strong sulphuric acid, tartaric acid and excess of ammonia are added, and the solution is poured into ammonium sulphide. Bismuth and copper sulphides are precipitated; the filtrate is acidified with acetic acid, giving a precipitate of antimony sulphide. The small fraction of earth acid occluded in the original sulphide precipitate is found in the filtrate from the antimony precipitate. Directions are given for the quantitative recovery of the earth acids.

XXIII. *The Quantitative Separation of Tantalum, Niobium, Titanium and Zirconium, and a new Analytical Grouping.* (Schoeller and Powell, *Analyst*, 1932, 57, 550.)—Our recently-published method for the separation of titanium from zirconium [XVIII.], based on precipitation of the titania as tannin complex from the nearly neutralised oxalate solution half-saturated with ammonium chloride, has now been proved to afford a quantitative separation of tantalum, niobium and titanium ("acid tannin group") from zirconium, thorium and aluminium ("basic tannin group"). Under the conditions realised by the procedure, tannin acts as a group reagent, precipitating any or all of the members of the acid tannin group, and thus separating them from any or all of the members of the basic tannin group. The inclusion of certain other metals (*e.g.*, uranium) in the last-named group is being investigated.

XXIV. *An improved Method for the Separation of Tantalum from Niobium.* (Schoeller, *Analyst*, 1932, 57, 750.)—An improved procedure for the separation of tantalum from niobium, based on fractional precipitation of the oxalate solution by tannin, is described. Four instances of the application of the method to mixtures of the two oxides in various proportions are recorded.

XXV. *The Separation of Uranium from Tantalum, Niobium and Titanium.* (Schoeller and Webb, *Analyst*, 1933, 58, 143.)—Like the earth acids and the earths in general, uranium is quantitatively precipitated by tannin from neutralised tartrate solution in presence of ammonium acetate and chloride. It is quantitatively precipitated from oxalate solution by tannin and a slight excess of ammonia. Uranium, like zirconium, thorium, aluminium and iron (Group *B*), can be quantitatively separated from tantalum, niobium and titanium (Group *A*) by tannin precipitation of the three last-named elements from feebly-acid oxalate solution half-saturated with ammonium chloride. In tartaric hydrolysis, uranium interferes with the normal course of precipitation in the case of niobium, but not of tantalum or of mixed pentoxides in which tantalic oxide preponderates.

XXVI. *The Interference of Tungsten in Earth-acid Determinations.* (Schoeller and Jahn, *Analyst*, 1934, 59, 465.)—When the earth acids are precipitated by tartaric hydrolysis, the co-precipitation of subordinate amounts of tungstic acid is incomplete. Neither tannin nor cupferron precipitates tungsten by itself from tartrate or oxalate solutions, but preponderating quantities of earth acid induce partial precipitation of tungsten. On account of its incomplete precipitation in all these procedures, we cannot

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yet assign to tungsten a definite position in our proposed analytical scheme. What we require is an additional method for the separation of tungsten from the earth acids as well as from other associated earths. A method to that end will shortly be published [XXIX.].

XXVII. *Observations on Manganese, and the Analysis of Tantalite.* (Schoeller and Webb, *Analyst*, 1934, 59, 667.)—Ammoniacal tartrate solutions of pure manganous salt were found to be readily precipitated by ammonium sulphide. On the other hand, the ammoniacal tartrate solutions obtained in the analysis of manganotantalite, when submitted to the same treatment, were incompletely precipitated—in a few of the tests hardly at all. An almost quantitative precipitation of manganous sulphide was, however, achieved after previous evaporation of the solutions to very small volume. No theoretical explanation for this erratic behaviour suggests itself. Manganese is precipitated from tartrate solution by tannin and an excess of ammonia. The precipitation is practically quantitative. A new process for the analysis of tantalite is described; it is based on the analytical methods elaborated in the course of these investigations.

XXVIII. *The Separation of the Rare Earths from the Earth Acids.* (Schoeller and Waterhouse, *Analyst*, 1935, 60, 284.)—For the separation of large quantities of rare earths from the earth acids, J. L. Smith's hydrofluoric-acid method is considered to be the best. The application of our tartaric-acid scheme to the soluble fluoride fraction obtained in Smith's method is an improvement on the original procedure.

Certain processes for the separation of small amounts of rare earths from much earth acid were studied. (1) Pied's proposed method (extraction of a bisulphate melt with oxalic acid solution) is not to be recommended except on a centigram scale. (2) The direct precipitation of the oxalates from a tartrate solution containing much earth acid is not suitable for the recovery of the rare earths; on a small scale, however (*i.e.*, with 0.02 g. or less of pentoxide), the method is quite satisfactory. (3) Tannin quantitatively precipitates the rare earths from ammoniacal tartrate solution; the precipitates are readily soluble in acetic acid. Tannin precipitation from feebly acid tartrate solution does not effect a clean-cut separation of the rare earths from the earth acids. (4) When the earth acids are precipitated by tartaric hydrolysis, the precipitate is quite free from rare earths. (5) We recommend the following separation process: precipitation of the bulk of the earth acids by tartaric hydrolysis, recovery of the

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rare earths and the balance of the earth acids by tannin precipitation from the ammoniacal filtrate, fusion of the ignited small tannin precipitate with bisulphate, and extraction of the melt with oxalic acid solution, or solution of the melt in tartaric acid and precipitation of the rare earths with oxalic acid.

XXIX. The Separation of Tungsten from Titanium, Niobium, Tantalum and Zirconium. (Powell, Schoeller and Jahn, *Analyst*, 1935, 60, 506.)—A separation of tungsten from titanium cannot be achieved by fusion of the mixed oxides with bisulphate and extraction of the melt with water or dilute acid. Fusion of the mixed oxides with sodium carbonate and extraction with water is likewise ineffective, but extraction of the carbonate melt with 10 per cent. sodium hydroxide solution affords a quantitative separation.

The only procedure found to separate tungsten from titanium and niobium, with or without tantalum and zirconium, consists in fusing the mixed oxides with potassium carbonate, and treating the aqueous extract of the melt with a slightly ammoniacal magnesium salt solution; the earths are precipitated, whilst alkali tungstate remains in solution. A repetition of the procedure is necessary unless the mixed earths contain a large proportion of niobic oxide; for accurate work, however, double treatment is recommended in all cases. Zirconia may be separated from tungstic oxide by fusion with alkali carbonate and extraction with water. The applicability of the methods available for the separation of tungsten from the individual earths and from the mixed earths is discussed. If the mixed earth acids are separated from tungsten by sodium-chloride precipitation [VI.], titration of the alkali in the precipitate furnishes a preliminary approximate determination of tantalum and niobium.

XXX. Observations on Beryllium. (Schoeller and Webb, *Analyst*, 1936, 61, 235.)—For the gravimetric determination of beryllia obtained by ammonia or tannin precipitation in presence of alkali sulphate, we fuse the ignited oxide with sodium carbonate and extract the fused mass with water, which leaves pure beryllia as an insoluble residue. The fusion process was first proposed by Wunder and Wenger for the separation of beryllia from alumina, a method which we, in common with several other investigators, regard as reliable.

Beryllia is quantitatively precipitated by tannin from ammoniacal tartrate solution. The earth-acid precipitate obtained by boiling the tartrate solution with excess of mineral acid (tartaric hydrolysis) does not occlude beryllia, if present. Tannin precipitation from oxalate solution half-saturated with ammonium

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chloride separates titanium, niobium and tantalum from beryllium as well as zirconium, thorium, aluminium, uranium, etc.

Up to the present, tartrate and acetate solutions do not appear to have proved suitable media for quantitative tannin separations. Uranium can be quantitatively separated from beryllium by precipitation as ferrocyanide; the slimy precipitate is readily filtered off and washed when mixed with pulped filter fibre.

XXXI. *The Determination of Tungsten in Earth-acid Minerals.* (Schoeller and Waterhouse, *Analyst*, 1936, 61, 449.)—The small amounts of tungsten frequently present in earth-acid minerals are precipitated with the earth acids by tartaric hydrolysis at fairly high concentration under standardised conditions, and are determined in the hydrolysis precipitate by the magnesia method. If the tungstic-oxide content of the mineral is high (the recorded maximum being about 3 per cent.), its determination by the proposed method involves a negative error increasing from about 0.0003 g. (with minerals high in tantalum) to about 0.002 g. (with minerals high in niobium or uranium). For high tungsten contents we recommend a correction factor, to be determined by experiment on a synthetic oxide mixture or on the earths recovered in the analysis. The inadequacy of certain qualitative tests for tungsten is briefly noticed.

XXXII. *Observations on Phosphorus, Vanadium and a Tannin Precipitation Series.* (Schoeller and Webb, *Analyst*, 1936, 61, 585.)—Phosphoric acid is occluded in the earth-acid precipitate produced by tartaric hydrolysis; it may be determined in the precipitate by fusion with sodium hydroxide, which produces soluble sodium phosphate and insoluble tantalate and niobate.

Tannin precipitation from oxalate solution half-saturated with ammonium chloride separates vanadium from titanium and tantalum, but not from niobium. Vanadium is not occluded in the earth-acid precipitate produced by tartaric hydrolysis, and is quantitatively precipitated by tannin from weakly-acid tartrate solution containing ammonium acetate. These reactions are utilised in a process for the separation of vanadium from tantalum and niobium.

A tannin precipitation series comprising ten elements is worked out, and certain conclusions deduced therefrom.

XXXIII. *General Summary and Conclusions.* (Schoeller, *Analyst*, 1936, 61, 806.)—This final section contains a classified index covering the thirty-two experimental sections, directions for the analysis of earth-acid minerals by the tartaric-acid method, and a brief summary of the main results of our investigations.

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